

# From Boron Trifluoride to Antimony Pentafluoride in Search of Stable Carbocations

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George A. Olah

University of Southern California, Los Angeles, California 90007, U. S. A.

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## The Search of Stable Carbocations

## I. Introduction

## 1. Personal Recollections of Hans Meerwein

Hans Meerwein was and always will be one of my heroes in chemistry. He introduced, ahead of Ingold and Robinson, the age of physical measurements into organic chemistry. At the same time his major aims always remained to find new methods and reactions of general synthetic utility. By his choice he was not interested in the synthesis of complex, large molecules, but in fundamental reactions and methods. He disliked narrow categories. He never considered himself to be a "physical organic" or "synthetic" chemist. He simply was a master chemist.

My first contact with Meerwein was in 1954 when I received, while still working in isolated Hungary, a letter from him. He had read a paper of ours, and offered useful comments, even pointing out that we had missed a relevant reference. We subsequently kept up correspondence. He continued to be interested in our early efforts to obtain long lived carbocations from alkyl (and acyl) fluorides in liquid boron trifluoride (and other Lewis acid halides) at low temperature, as well as via metathetic reactions of organic halides with silver tetrafluoroborate (a reagent we introduced in 1955 for the ionization of bromocyclohexadienes to form benzenium ions and which Meerwein developed to a wide utility alkylation method).

It was in 1959 when I was first able to meet Meerwein personally during a visit to Marburg. He was at the time 79 but I would have thought him to be 20 years younger. He was not only extremely interested and up-to-date in chemistry, full with exciting, inventive ideas, but was even busy at the laboratory bench! His undiminished interest in chemistry and productivity well into his eighties is by now legendary. He maintained to the last an amazing knowledge and love of chemistry. He will always remain a shining example and great inspiration for future generations of chemists. It was indeed a great privilege to have visited him on a number of subsequent occasions, the last in the summer of 1965, shortly before his death. It was particularly rewarding for me to be able to give in his presence at that occasion a comprehensive report of our work on stable carbocations in antimony pentafluoride containing superacids. Meerwein actively participated in the discussion and his generous concluding remarks at the end of the Colloquium were that the search for carbocations, including the elusive alkyl cations, which started with boron trifluoride came to a successful end with antimony pentafluoride. This is then, in Meerwein's words, the topic which I will be reviewing dedicated to the memory of the pioneer and master of ionic organic chemistry.

## 2. General Concepts of Carbocations

Electrophilic reactions are generally considered<sup>1)</sup> to proceed through cationic (i. e., *carbocationic*) intermediates. The general concept<sup>1-3)</sup> of *carbocations* encompasses all cations of carbon containing compounds which sometimes were differentiated into two limiting classes: trivalent ("classical") carbenium ions and five or higher coordinated ("non-classical") carbonium ions. Whereas the differentiation of limiting

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trivalent carbenium, and pentacoordinated carbonium ions serves a useful purpose to establish the significant differences between these ions, it is also clear that in most specific systems there exists a continuum of charge delocalization. In fact in all carbocations (even in the parent  $\text{CH}_3^+$ ) there is a continuum of the degree of charge delocalization, and thus to think in limiting terms is rather meaningless. Participation by neighboring groups can not only be by  $n$ - and  $\pi$ -donors, as most generally recognized, but also by  $\sigma$ -ligands. There is in principle no difference between these.  $\sigma$ -Participation in properly oriented systems is not only possible, but it is unavoidable. The only question is its degree, and not whether it exists<sup>4)</sup>.

As is well known, trivalent carbenium ions play an important role in electrophilic reactions of  $\pi$ - and  $n$ -donor systems. Similarly, pentacoordinated carbonium ions are the key to electrophilic reactions of  $\sigma$ -donor systems (single bonds). The ability of single bonds to act as  $\sigma$ -donor lies in their ability to form carbonium ions via triangular two electron, three-center bond formation. Consequently, there seems to be in principle no difference between the electrophilic reactions of  $\pi$ - and  $\sigma$ -bonds except that the former react more easily even with weak electrophiles, whereas the latter necessitate more severe conditions. The role of carbocations in electrophilic reactions of  $\pi$ - and  $\sigma$ -donor systems is well recognized!

The concept of carbocations (the logical and now IUPAC recommended name for all cationic carbon compounds since the negative ions are called *carbanions*), with exception of the early isolation of highly stabilized triarylmethyl cation salts, grew to maturity through kinetic, stereochemical and product studies of a wide variety of reactions, especially unimolecular nucleophilic substitutions and eliminations. Leading investigators like Meerwein, Ingold, Hughes, Whitmore, Bartlett, Nenitzescu, Winstein, and others have contributed fundamentally to the development of modern carbocation theory<sup>2)</sup>, e. g., the concept of electron deficient cationic intermediates. Direct observation of stable, long-lived carbenium ions, generally in highly acidic (superacid) solvent systems has become possible only in recent years<sup>1)</sup>.

Based on our continuing study of carbocations by direct observation of long-lived species, it became increasingly apparent that the carbocation concept is much wider than previously realized, and necessitated a general definition<sup>1)</sup>. Therefore, such a definition was offered based on the realization that two distinct, limiting classes of carbocations exist:

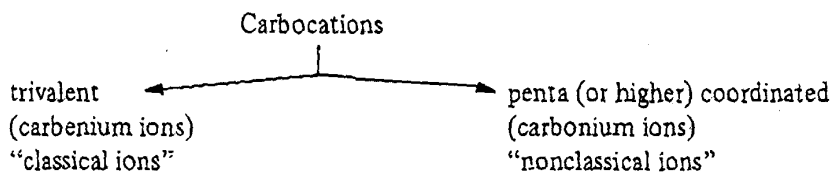
a) Trivalent ("classical") carbenium ions contain an  $\text{sp}^2$ -hybridized electron deficient carbon atom, which tends to be planar in the absence of constraining skeletal rigidity or steric interference. (It should be noted that  $\text{sp}$ -hybridized, linear oxocarbonium ions and vinyl cations also show substantial electron deficiency on carbon). The carbenium carbon contains six valence electrons, thus is highly electron deficient. The structure of trivalent carbocations can always be adequately described by using two-electron two-center bonds (Lewis valence bond structures).

b) The bonding nature of penta- (or higher) coordinated ("nonclassical") carbonium ions, which contain five or (higher) coordinated carbon atoms, cannot be described by two-electron single bonds alone, but also necessitates the use of two-electron, three (or multi) center bond(s). The carbocation center is always surrounded by eight electrons, although two (or more) of them are involved in multi-

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center bonds, and the ions overall are electron deficient (due to electron sharing of two binding electrons between three (or more) centers).

Lewis's concept that a chemical bond consists of a pair of electron shared between two atoms became the foundation of structural chemistry and chemists still tend to brand some compounds as anomalous compounds whose structures cannot be depicted in terms of such bonds alone. Carbocations with too few electrons to allow a pair for each "bond", came to be referred to as "nonclassical", a label still used even though it is now recognized that, like any other substances, they adopt the structures appropriate for the number of electrons they contain.



Expansion of the carbon octet via 3d-orbital participation does not seem possible; there can be only eight valence electrons in the outer shell of carbon<sup>5)</sup>. Thus, the covalency of carbon cannot exceed four. Penta- (or high)-coordination implies a species with five (or more) ligands within reasonable bonding distance from the central atoms<sup>6)</sup>. The transition states long ago suggested for  $S_N2$  and  $S_E2$  reactions may represent such cases. However, the direct observation of stable penta- (or higher) coordinated species in solution was not reported until recent studies of long-lived "nonclassical" ions in superacid solvent systems. Moreover,  $S_E2$  substitution reactions have been, in the past, mainly restricted to organometallic compounds, *i. e.*, organomercurials<sup>7)</sup>.

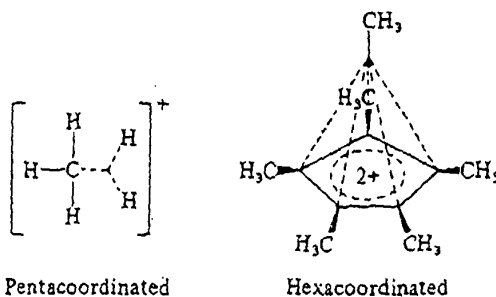
Neighboring group interactions with the vacant p-orbital of the carbenium ion center can contribute to ion stabilization via charge delocalization. Such phenomena can involve atoms with unshared electron pairs (*n*-donors) C-H and C-C hyperconjugation, bent  $\sigma$ -bonds (as in cyclopropylcarbenium ions) and  $\pi$ -electron systems (direct conjugative or allylic stabilization). Thus trivalent carbenium ions can show varying degrees of delocalization without becoming pentacoordinated carbonium ions. The limiting classes defined do not exclude varying degrees of delocalization, but in fact imply a spectrum of carbocation structures.

In contrast to the rather well-defined trivalent ("classical") carbenium ions, "nonclassical ions"<sup>8)</sup> have been more loosely defined. In recent years, a lively controversy has centered on the classical-nonclassical carbonium ion problem<sup>9)</sup>. The extensive use of "dotted lines" in writing carbonium ion structures has been (rightly) criticized by Brown<sup>9d)</sup>, who carried, however, the criticism to question the existence of any  $\sigma$ -delocalized (nonclassical) ion. For these ions, if they exist, he stated "... a new bonding concept not yet established in carbon structures is required."

Clear, unequivocal experimental evidence has by now been obtained for non-classical ions such as the norbornyl cation<sup>10)</sup>. The bonding concept required to define "nonclassical ions" is simply to consider them as penta- (or higher coordi-

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nated) carbonium ions, of which  $\text{CH}_5^+$  (the methonium ion-carbonium ion) is the parent, as  $\text{CH}_3^+$  (methenium ion, methyl cation, carbenium ion) is the parent for trivalent carbenium ions. An example of a hexacoordinated carbonium ion is the pyramidal dication of Hogeveen's<sup>11)</sup>.



Concerning the carbocation concept, it is regrettable that in the Anglo-Saxon literature the general usage for a long time named the trivalent, planar ions of the  $\text{CH}_3^+$  type as *carbonium ions*. If the name is considered analogous to other *onium ions* (ammonium, sulfonium, phosphonium ions, etc.), then it should relate to the higher valency state carbocation. The higher valency state carbocations, however, clearly are not the trivalent but the *penta (or higher) coordinated cations*. The German and French literatures indeed frequently use the "carbenium ion" naming for the trivalent cations. If we consider these latter ions as protonated carbenes, the naming is indeed correct<sup>12)</sup>. It should be pointed out, however, that the "carbenium ion" naming depicts only trivalent ions and thus should not be a general name for *all* carbocations. IUPAC's Organic Chemistry Division recently reviewed the nomenclature of physical organic chemistry, and recommends the use of the "carbocation" for naming all positive ions of carbons. "Carbenium" or "carbonium ion" naming, similar to the "carbinol" naming of alcohols, is discouraged.

### 3. Development of the Carbocation Concept: Kinetic and Stereochemical Studies

One of the most audacious and fruitful ideas born in organic chemistry was the suggestion that carbocations might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products. It was Hans Meerwein<sup>13)</sup> who in 1922, while studying the kinetics of the rearrangement of camphene hydrochloride to isobornyl chloride reported the important observation that the reaction rate increased in a general way with the dielectric constant of the solvent. Further, he found that metallic chlorides – such as  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , and  $\text{SbCl}_3$  (but not  $\text{BCl}_3$  or  $\text{SiCl}_4$ ), as well as dry  $\text{HCl}$  – which promote the ionization of triphenylmethyl chloride by formation of ionized complexes, considerably accelerate the rearrangement of camphene hydrochloride. Meerwein concluded that the conversion of camphene hydrochloride to isobornyl chloride actually does not proceed by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. Thus, the modern concept of carbocation intermediates was born.

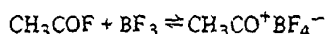
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Ingold, Hughes, and their collaborators in England, starting in the late 1920's carried out detailed kinetic investigations on what later became known as nucleophilic substitution at saturated carbon and polar elimination reactions<sup>14)</sup>. The well-known work relating to S<sub>N</sub>1 and later E1 reactions established the carbocation concept in these reactions. Whitmore<sup>15)</sup>, in a series of papers which began in 1932, generalized Meerwein's rearrangement theory to many organic chemical reactions.

*Kinetic and stereochemical* evidence helped to establish carbocation intermediates in organic reactions. These species, however, were generally too short lived and could not be directly observed by physical means.

## II. Observation of Stable, Long Lived Carbocations

The transient nature of carbocations arises from their extreme reactivity with nucleophiles. The use of low nucleophilicity gegenions, particularly tetrafluoroborates (BF<sub>4</sub><sup>-</sup>) enabled Meerwein in the forties to prepare a series of oxonium and carboxonium ion salts, such as R<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> and HC(OR)<sub>2</sub><sup>+</sup> respectively. These Meerwein salts are effective alkylating agents, and transfer alkyl cations in S<sub>N</sub>2 type reactions. However, simple alkyl cation salts (R<sup>+</sup>BF<sub>4</sub><sup>-</sup>) were not obtained in Meerwein's studies. The first acyl tetrafluoroborate, i. e. acetylum tetrafluoroborate was obtained by Seel<sup>16)</sup> in 1943 by reacting acetyl fluoride with boron trifluoride at low temperature.



In the early fifties we started a study of the intermediates of Friedel-Crafts reactions and inter alia carried out a systematic investigation of acyl fluoride-boron trifluoride complexes. We were also to observe a series of donor-acceptor complexes as well as stable acyl cations. Subsequently the investigations were also extended to other Lewis acid halides. In the course of these studies we also increasingly became interested in alkyl halide-Lewis acid halide complexes. The study of alkyl fluoride-boron trifluoride complexes by electric conductivity measurements indicated the formation of ionic complexes in the case of tertiary butyl and isopropyl fluorides at low temperature, whereas methyl and ethyl fluoride ions formed molecular coordination complexes. It was, the nucleophilicity of the system which prevented in isolating or to otherwise characterize alkyl cation salts. It was for this reason that we initiated a systematic study of more suitable acid and low nucleophilicity solvent systems. This resulted in the discovery of superacidic systems and very weakly nucleophilic solvents, which finally allowed to obtain alkyl cations as stable, long lived species<sup>1)</sup>. Subsequently, a wide range of practically all conceivable carbocations became readily available for structural and chemical studies<sup>1, 2)</sup>.

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## A. Trivalent Carbocations

### 5. Alkyl Cations

*a. Early Unsuccessful Attempts.* Simple alkyl cations were considered until the early sixties only as transient species<sup>2)</sup>. Their existence has been inferred from the study of the course of certain reactions. No reliable physical measurements, other than electron impact measurements of the simple alkyl cations were known. The formation of gaseous organic cations under electron bombardment of alkanes, haloalkanes, and other precursors has been widely investigated in mass spectrometric studies<sup>17)</sup>. No similar direct observation of carbocations in solution was achieved.

The observation of alkyl cations like that of tert-butyl cation (trimethylcarbenium ion),  $(\text{CH}_3)_3\text{C}^+$  1 or the isopropyl cation (dimethylcarbenium ion),  $(\text{CH}_3)_2\text{CH}^+$  2 thus was a longstanding challenge. The existence of alkyl cations in systems containing alkyl halides and Lewis acid halides has been inferred from a variety of observations, such as vapor pressure depressions of  $\text{CH}_3\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Cl}$  in the presence of gallium chloride<sup>18)</sup>; conductivity of aluminium chloride in alkyl chlorides<sup>19)</sup> and of alkyl fluorides in boron trifluoride<sup>20)</sup>; as well as the effect of ethyl bromide on the dipole moment of aluminium bromide<sup>21)</sup>. However, in no case had well-defined, stable alkyl cation complexes been established even at very low temperatures.

Electronic spectra of alcohols and olefins in strong proton acids ( $\text{H}_2\text{SO}_4$ ) were obtained by Rosenbaum and Symons<sup>22)</sup>. They observed, for a number of simple aliphatic alcohols and olefins, absorption maximums around 290 nanometers and ascribed this absorption to the corresponding alkyl cations.

Finch and Symons<sup>23)</sup>, on reinvestigation of the absorption of aliphatic alcohols and olefins in sulfuric acid solution, showed that the condensation products formed with acetic acid (used as solvent for the precursor alcohols and olefins) were responsible for the spectra, not the simple alkyl cations. Moreover, protonated mesityl oxide was identified as the absorbing species in the system of isobutylene, acetic acid, and sulfuric acid.

Deno and his co-workers<sup>24)</sup> carried out an extensive study of the fate of alkyl cations in undiluted  $\text{H}_2\text{SO}_4$  and oleum produces equal amounts of a saturated hydrocarbon mixture ( $\text{C}_4$  to  $\text{C}_{18}$ ) insoluble in  $\text{H}_2\text{SO}_4$  and a mixture of cyclopentenyl cations ( $\text{C}_9$  to  $\text{C}_{20}$ ) in the  $\text{H}_2\text{SO}_4$  layer. These cations exhibit strong ultraviolet adsorption around 300 nm.

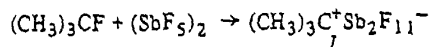
It must therefore be concluded that earlier attempts to prove the existence of stable, well-defined alkyl cations were unsuccessful in experiments using sulfuric acid solutions and inconclusive in the interaction of alkyl halides with Lewis acid halides. Proton elimination reactions or dialkyl halonium ion formation may have affected conductivity studies.

*b. Preparation from Alkyl Fluorides in Antimony Pentafluoride Solution.* In 1962 we first directly observed stable alkyl cations in solution<sup>25-27)</sup>. We obtained the *t*-butyl cation 1 (trimethylcarbenium ion) when *t*-butyl fluoride was dissolved in excess antimony pentafluoride, which served both as Lewis acid and solvent. Later



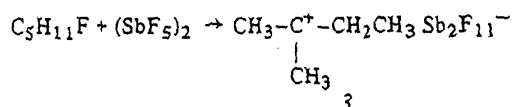
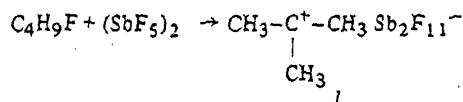
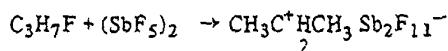
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the counter ion was found to be, under these conditions, primarily the dimeric  $\text{Sb}_2\text{F}_{11}^-$  anion<sup>28</sup>); whereas in  $\text{SbF}_5\text{--SO}_2$  or  $\text{SbF}_5\text{--SO}_2\text{ClF}$  solutions,  $\text{SbF}_6^-$  and  $\text{Sb}_2\text{F}_{11}^-$  are both formed.



The possibility of obtaining stable alkyl fluoroantimonate salts from alkyl fluorides (and subsequently other halides) in antimony pentafluoride solution (neat or diluted with sulfur dioxide, sulfuryl chloride fluoride, or sulfuryl fluoride) or in other superacids<sup>29</sup> such as  $\text{FSO}_3\text{H--SbF}_5$  (Magic Acid<sup>R</sup>,<sup>30</sup>  $\text{HF--SbF}_5$  (fluoroantimonic acid),  $\text{HF--TaF}_5$  (fluorotantalic acid) and the like was evaluated in detail, extending studies to all isomeric  $\text{C}_3$  to  $\text{C}_8$  alkyl halides, as well to a number of higher homologs<sup>31-32</sup>).

Propyl, butyl, and pentyl fluorides with antimony pentafluoride gave the isopropyl, t-butyl and t-amyl cations (as their fluoroantimonate salts) 2, 1 and 3.



The secondary butyl and amyl cations can be observed only at very low temperatures and they rearrange readily to the more stable tertiary ions.

Generally, the most stable tertiary or secondary carbocations are observed from any of the isomeric alkyl fluorides in superacidic solvent system.

*c. Nuclear Magnetic Resonance Spectra.* One of the most powerful tools in the study of carbocations is nuclear magnetic resonance spectroscopy. The main feature

Table 1. Characteristic PMR<sup>a</sup> Parameters of alkyl cations in  $\text{SbF}_5\text{--SO}_2\text{ClF}$  solution at  $-70^\circ$

Ion		$\delta_{\text{H}}$				
		$\text{CH}^+$	$J_{\text{CH}}$	$J_{\text{CCH}}$	$\alpha\text{--CH}_2$	$\alpha\text{--CH}_3$ $\beta\text{--CH}_3$
$(\text{CH}_3)_2\text{CH}^+$	2	13	169	3.3		4.5
$(\text{CH}_3)_3\text{C}^+$	1			3.6		4.15
$(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$	3				4.5	4.1   1.94
$\text{CH}_3\text{C}^+(\text{CH}_2\text{CH}_3)_2$	4				4.44	4.16   1.87

<sup>a</sup> Chemical shifts are in ppm from external capillary TMS. Coupling constants are in Hz.

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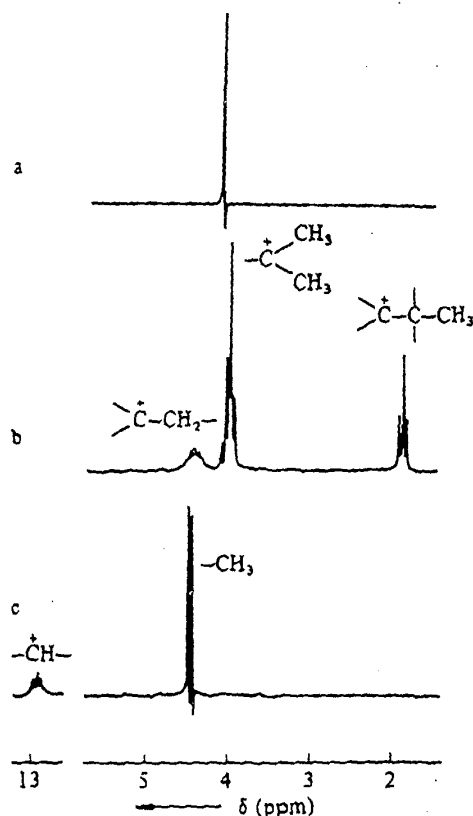


Fig. 1.  $^1\text{H}$ -NMR spectra of: a) the *tert*-butyl cation (2) [trimethylcarbenium ion,  $(\text{CH}_3)_3\text{C}^+$ ]; b) the *tert*-amyl cation (3) [dimethylethylcarbenium ion,  $(\text{CH}_3)_2\text{C}^+-\text{C}_2\text{H}_5$ ]; c) the isopropyl cation (1) [dimethylcarbenium ion,  $(\text{CH}_3)_2\text{C}^+\text{H}$ ]. (60 MHz,  $\text{SbF}_5-\text{SO}_2\text{ClF}$  solution.  $-60^\circ\text{C}$ )

of the proton NMR spectra of alkyl fluorides in antimony pentafluoride is the substantial deshielding of the protons in the carbocations as compared with the starting alkyl fluorides (Fig. 1 and Table 1).

In Order to prove that stable alkyl cations, and not exchanging donor-acceptor complexes were obtained, we also investigated the  $^{13}\text{C}$  nuclear magnetic resonance of the potentially electropositive carbenium carbon atom in alkyl cations<sup>31-32</sup>.

The  $^{13}\text{C}$  shift in the *t*-butyl cation  $(\text{CH}_3)_3^{13}\text{C}^+$  1 in  $\text{SO}_2\text{ClF}-\text{SbF}_5$  solution at  $-20^\circ$  is at  $\delta_{13\text{C}}$  335.2 (all CMR shifts are from  $^{13}\text{C}$  TMS) with a long-range coupling to the methyl protons of 3.6 Hertz.

The  $^{13}\text{C}$  shift in the isopropyl cation 2 under identical conditions, is  $\delta_{13\text{C}}$  320.6 with a long-range coupling to the methyl protons of 3.3 hertz. The direct  $^{13}\text{C}-\text{H}$  coupling is 169 hertz (indicating  $sp^2$  hybridization of the carbenium carbon atom), while the long-range, proton-proton coupling constant is 6.0 Hertz (see Fig. 1).

Substitution of the methyl group in the *t*-butyl cation by hydrogen thus causes an upfield shift of 10.4 ppm. Although the CMR shift of the carbocation center of the *t*-butyl cation is more deshielded than that of the isopropyl cation (by about 10 ppm), this can be explained by the methyl substituent effect, which may amount to 22 ppm. The tertiary butyl cation thus is more delocalized and stable than the secondary isopropyl.

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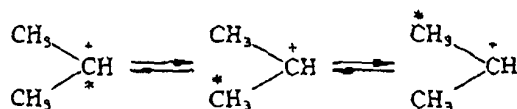
The  $^{13}\text{C}^+$  shift in the *t*-amyl cation  $\text{C}_2\text{H}_5\text{C}^+(\text{CH}_3)_2$  3 is at  $\delta^{13}\text{C}$  335.4 which is similar to that of *t*-butyl cation. The shift difference is much smaller than the 17 ppm found in the case of the related alkanes, although the shift observed is in the same direction. The  $^{13}\text{C}$  NMR chemical shifts and coupling constants  $J_{\text{C-H}}$  of  $\text{C}_3\text{-C}_8$  alkyl cations 1-13 are shown in Tables 2 and 3<sup>32)</sup>.

It is difficult to interpret these large deshieldings in any way other than as a direct proof that

- (i) the state of hybridization of the carbon atoms involved in the carbenium ions is  $sp^2$ ; and
- (ii) at the same time, the carbon atom carries a substantial positive charge.

Table 1 summarizes the  $^1\text{H}$  and  $^{13}\text{C}$  NMR parameters for the carbocations center in a series of selected secondary and tertiary carbenium ions. Data are characterized by substantial deshielded chemical shifts with coupling constant ( $J_{\text{CH}}$ ) that indicate  $sp^2$ -hybridization.

When the isopropyl cation 2 was generated from 2-chloropropane with 50 percent  $^{13}\text{C}$  enrichment of C-2 in  $\text{SO}_2\text{ClF-SbF}_5$  at 60 °C, equilibration of the  $^{13}\text{C}$  label occurred with a half-life of 1 hour. After several hours, the  $^{13}\text{C}$  was distributed equally among the three carbons. This observation suggests involvement of protonated cyclopropanes in the carbon scrambling process (see subsequent discussion). Similar scrambling was observed in the secondary butyl 14 (*sec*-butyl) and *t*-amyl cations 4 (Saunders)<sup>33)</sup>.



*d. Infrared and Raman Spectra.* Infrared and Raman spectra of the stable alkyl carbocations were also observed<sup>26, 34)</sup> and are in complete agreement with the carbenium structure of the ions. Infrared spectra of these ions and of their deuterated analogs correspond to the spectra predicted by calculations based on molecular models and force constants. Thus, vibrational spectra can also be used in the identification of stable carbenium ions.

Laser Raman spectroscopy, particularly with helium-neon lasers, is another powerful tool in the study of carbocations. Because Raman spectra give valuable information on symmetry, these spectra help to establish, in detail, structures of the ions and their configurations. The Raman spectroscopic data provide strong evidence that the *t*-butyl cation 1 in magic acid<sup>30)</sup> solution prefers a conformation leading to overall  $\text{C}_{3v}$  point group symmetry (Table 4 and Fig. 2). Thus the  $\text{C}^+(\text{CH}_3)_3$  ion exists in these solutions with a planar  $\text{C}^+(\text{C}_3)$  carbon skeleton and with one hydrogen atom of each  $\text{CH}_3$  group above the  $\text{C}^+-\text{C}_3$  plane. The other two hydrogen atoms are arranged symmetrically below the  $\text{C}^+\text{C}_3$  plane to the right and left of the  $\text{C}_3$  axis. Raman spectra observed for the *t*-amyl cation, the pentamethylethyl cation, and the tetramethylethyl cation also show similar structure. The Raman spectroscopic studies thus provide, in addition to  $^{13}\text{C}$  NMR data, direct evidence for the planar carbenium center of alkyl cations.

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Table 2.  $^{13}\text{C}$  chemical shifts of the static  $\text{C}_3$  to  $\text{C}_8$  alkyl cations

Cation	1 <sup>a</sup>	2	3	4	5	6	7	8
	51.5 (q)	320.6 (s)						
	47.5 (q)	335.2 (s)						
	44.6 (q)	335.4 (s)	57.5 (t)	9.3 (q)				
	41.9 (q)	336.4	54.5 (t)	8.9 (q)				
	45.0 (q)	333.4	64.4 (t)	20.9 (t)	12.6 (q)			
	44.9 (q)	332.9 (s)	62.8 (t)	29.3 (t)	22.6 (t)	13.0 (q)		
	42.1 (q)	334.7 (s)	55.1 (t)	9.1 (q)	61.6 (t)	20.2 (t)	12.5 (q)	

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## The Search of Stable Carbocations

	8	45.4 (q)	332.1 (s)	70.1 (t)	31.4 (d)	21.7 (q)	
	9		336.8 (s)	51.8 (t)	8.6 (q)		
	10	44.6 (q)	332.5 (s)	62.7 (t)	27.4 (t)	31.1 (t)	13.1 (q)
	11		334.7 (s)	51.6 (t)	8.1 (q)	58.8 (t)	11.6 (q)
	12	42.0 (q)	334.3 (s)	54.7 (t)	8.7 (q)	59.7 (t)	12.9 (q)
	13	42.1 (q)	332.8 (s)	61.9 (t)	19.7 (t)	12.1 (q)	

31 a All chemical shifts are measured from external Me<sub>4</sub>Si.


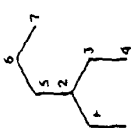

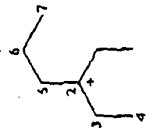
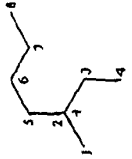
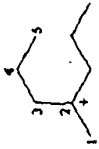
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Table 3.  $^{13}\text{C}-\text{C}-\text{H}$  coupling constants of the static  $\text{C}_3$  to  $\text{C}_8$  alkyl cations

	1	2	3	4	5	6	7	8
	131.7 <sup>a</sup>	171.3						
	130.8							
	131.8		127.4	130.8				
	131.7		124.8	129.6				
	132.1		126.6	131.8	129.1			
	131.4		126.7	131.4	127.5	126.2		
	131.5		124.0	128.8	119.2	126.2	123.9	

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	131.6	124.7	137.2	124.1	
		123.2	129.8		
	131.4	127.2	~131	~131	126.4
		121.6	130.3	121.1	124.3
	132.5	~122	129.2	122.4	127.0
	129.0	126.2	132.5	129.5	

a All values are measured in hertz.

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Table 4. Raman and IR frequencies of the *tert*-butyl cation and  $[\text{D}_9]\text{-tert-butyl}$  cation and their correlation with those of  $(\text{CH}_3)_3\text{B}$  and  $(\text{CD}_3)_3\text{B}$ 

Species	Frequency of vibration ( $\text{cm}^{-1}$ )											
	$\nu_1, \nu_{12}, \nu_7, \nu_{19}$	$\nu_2, \nu_{13}$	$\nu_{21}$	$\nu_{14}$	$\nu_{15}$	$\nu_{17}$	$\nu_5$	$\nu_{16}$	$\nu_6$	$\nu_9$	$\nu_{10}$	$\nu_{18}$
$(\text{CH}_3)_3\text{C}^{\oplus}$ (2)	2947	2850		1450		1295			667		347	306
$(\text{CH}_3)_3\text{B}$	2975	2875	1060	1440	1300	1150	906	866	675	973 (486?)	336 <sup>a</sup>	320
$(\text{CD}_3)_3\text{C}^{\oplus}$	2187	2090		1075		980			720		347	300
$(\text{CD}_3)_3\text{B}$	2230	2185		1033	1018	1205			620	870	(289) <sup>b</sup>	(276) <sup>b</sup>

<sup>a</sup> IR frequency.<sup>b</sup> Calculated.



## The Search of Stable Carbocations

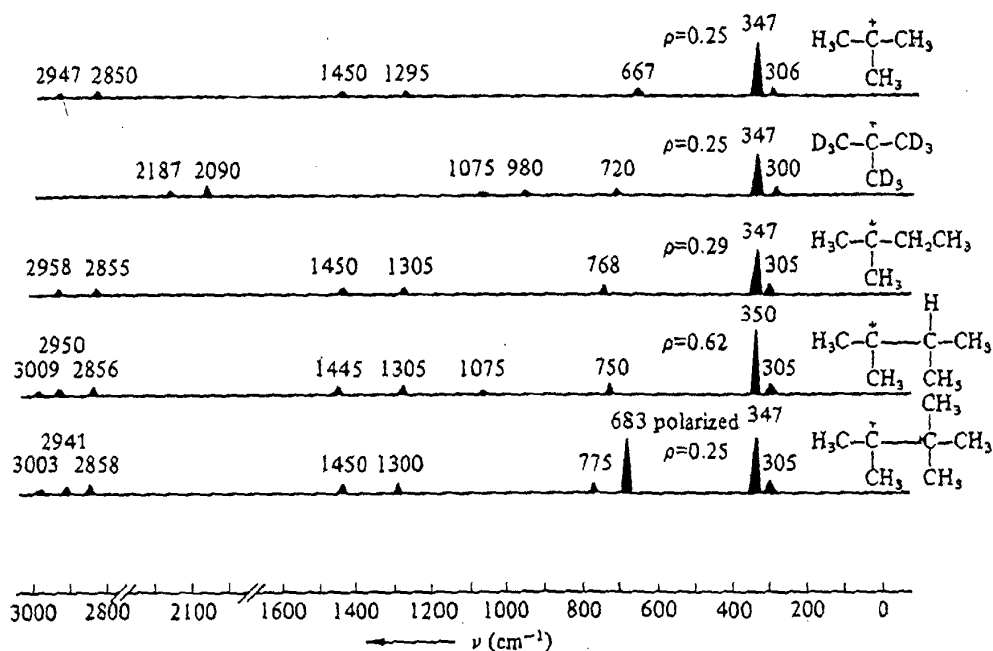


Fig. 2. Schematic representation of Raman spectra of alkyl cations

Evidence for planarity or near planarity of the  $\text{sp}^2$  center of trivalent alkyl cations thus comes from the combined results of NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) IR, and Raman spectroscopy<sup>31-32, 34</sup>.

*e. Electronic Spectra.* The observations of stable alkyl cations in antimony pentafluoride solutions also opened up the possibility of investigating the electronic spectra of these solutions. We have reported<sup>35</sup> that solutions of alkyl cations in  $\text{FSO}_3\text{H}-\text{SbF}_5$  solution at  $-60^\circ\text{C}$  showed no absorption maxima above 210 nm. In view of this observation, it was resolved that previous claims relating to a 290 nm absorption of alcohols and olefins in sulfuric acid solution were due to condensation products or cyclic allylic ions and not to the simple alkyl cations<sup>36</sup>.

*f. X-Ray Photoelectron (ESCA) Spectra.* X-Ray photoelectron spectroscopy (ESCA)<sup>37</sup> is an extremely useful method for the investigation of carbocations<sup>38</sup>. Within such molecules the formal charge is generally unequally shared by different atoms. Consequently, the core electrons of these atoms are differently screened and show increasing binding energies with increasing positive charge localization. In the latter cases the energy differences are large enough to give rise to separate K-shell photoelectron lines.

In contrast measurements of carbon 1s electron binding energies in several hydrocarbons yielded a rather narrow range of chemical shifts. For instance, one cannot make a distinction between the carbon atoms of neopentane and those of benzene because their 1s binding energies are virtually the same (290.4 eV). Ethane

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(290.6), ethylene (290.7), and acetylene (291.2 eV) carbon 1s binding energy differences are also very small. These results are in agreement with theoretical expectations. Core electrons are barely affected unless their screening against nuclear attraction is modified by a significant change in the outer (valence) electron shell. In other words, core electron binding energies are mainly dependent on the formal charge of the corresponding atom and on the electronegativity of attached atoms or groups of atoms. The fact that such factors are minimal in hydrocarbons accounts for the small differences described above.

Electron spectra of carbenium ions were obtained in frozen superacid solutions or as isolated salts, generally in a 1 : 1 (v/v)  $\text{SbF}_5$ - $\text{SO}_2$  solution. Sulfur dioxide was subsequently removed by the usual freeze-thaw procedure. A thin layer of the viscous  $\text{SbF}_5$  solution was deposited on the precooled sample holder, in a dry nitrogen atmosphere. The spectra are recorded at liquid nitrogen temperature<sup>38</sup>.

The binding energies  $E_b$  (defined as differences between the Fermi level and the 1s atomic level energies) are given by the equation

$$E_b = E_{h\nu} - E_k - \phi_s$$

where  $E_{h\nu}$  is the energy (1485.6 eV) of the exciting radiation (Al K $\alpha$  X-rays),  $E_k$  is the measured kinetic energy of the photoejected electron, and  $\phi_s$  is the spectrometer work function (the energy necessary to bring the electron from the Fermi level to the free-electron level). The photoelectron spectrum of *tert*-butyl cation 1 is shown in Fig. 3.

The lower traces in Fig. 3 represent the result given by a curve resolver. The peak area ratio is 1 : 3.

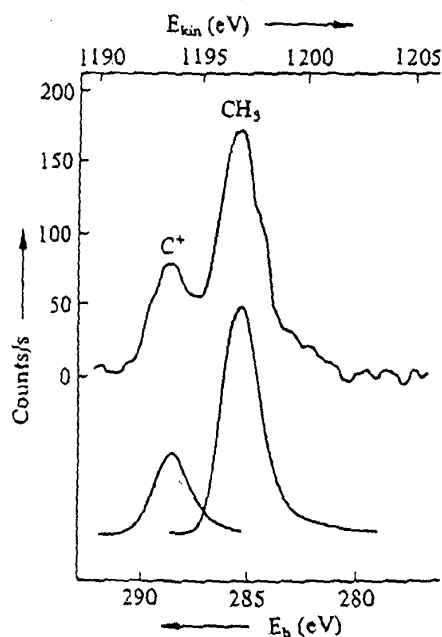
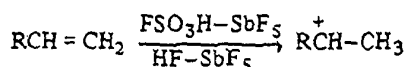


Fig. 3. Carbon 1s photoelectron spectrum of *tert*-butyl cation 1

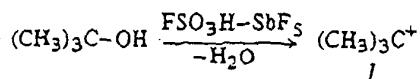
## The Search of Stable Carbocations

The experimental carbon 1s binding energy difference (3.9 eV) between the carbenium ion center and the remaining three carbon atoms is in the limit of that predicted by *ab initio* calculation (4.45 eV). Comparable results were obtained for the *t*-amyl cation ( $dE_{6+C-C} = 4 \pm 0.2$  eV).

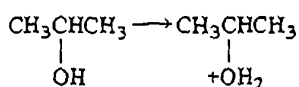
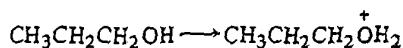
*g. Preparation from Other Precursors.* Alkyl cations can be formed not only from halide precursors (the earlier investigation of generation from alkyl fluorides was later extended to alkyl chlorides, bromides, and even iodides), but also from olefins in superacids like  $\text{HF-SbF}_5$ <sup>37, 38</sup>.



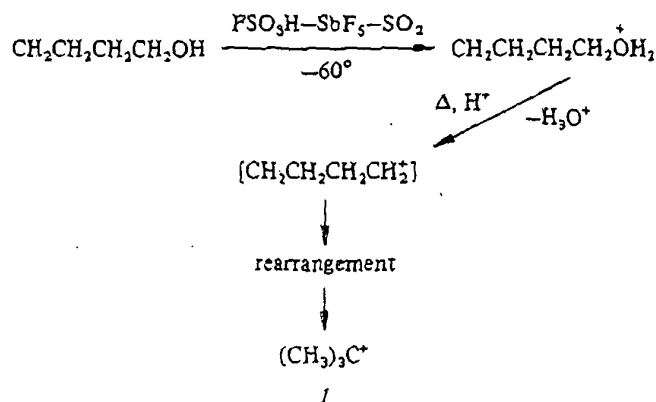
Tertiary and reactive secondary alcohols in superacids like  $\text{FSO}_3\text{H-SbF}_5$  ("magic acid"<sup>30, 36</sup>)  $\text{FSO}_3\text{H}$ , and  $\text{SbF}_5\text{-SO}_2\text{-(SO}_2\text{ClF)}$  also ionize to the corresponding carbocations<sup>41</sup>. The generation of alkyl cations from alcohols indicates the great advantages of increasing acidity and of using acid systems with low freezing points. Deno showed that the use of sulfuric acid and oleum results in formation of cyclized allylic ions from simple aliphatic alcohols<sup>24</sup>. With the use of extremely strong acid,  $\text{FSO}_3\text{H-SbF}_5$ , tertiary and many secondary alcohols can be ionized to the corresponding alkyl cations.



Primary and less reactive secondary alcohols are protonated in  $\text{FSO}_3\text{H-SbF}_5$  solution at low temperatures ( $-60^\circ$ ) and show very slow exchange rates<sup>42</sup>.

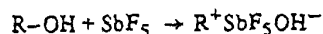


Temperature-dependence studies of the NMR spectra of protonated alcohols allow the kinetics of dehydration to be followed<sup>43</sup>.

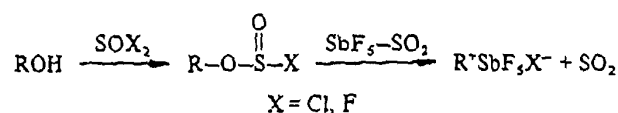
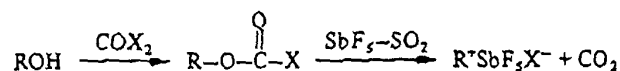


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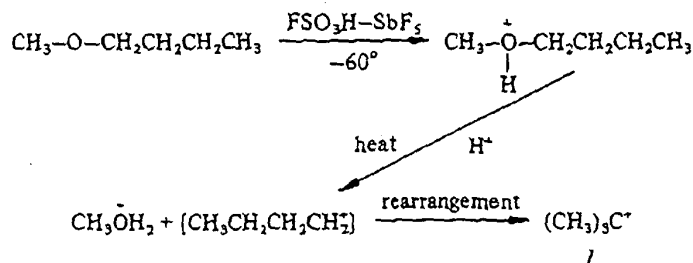
Antimony pentafluoride itself (neat or in  $\text{SO}_2$  or  $\text{SO}_2\text{ClF}$  solution) ionizes alcohols to form alkyl carbocations.



To overcome difficulties and achieve ionization of primary (and less reactive secondary) alcohols at low temperatures, we found, in some cases, that it is advantageous to transfer them with thionyl halides or carbonyl halides to the corresponding haloformates or halosulfites. These in turn ionize readily in  $\text{SbF}_5\text{-SO}_2$  solution and lose  $\text{CO}_2$  or  $\text{SO}_2$  <sup>39, 44</sup>.

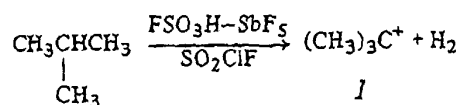


Aliphatic ethers are protonated in strong acids, and, at low temperatures, the exchange rates of the acidic proton are slow enough to permit direct observation by NMR spectroscopy <sup>45</sup>. Temperature dependent NMR spectral studies allow one to follow the kinetics of ether cleavage to form alkyl reactions.

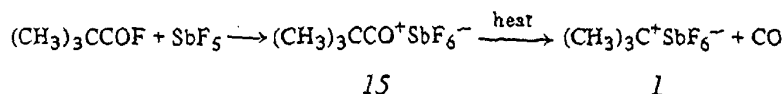


Protonation and ionization of mercaptans (thiols) and sulfides were similarly studied <sup>46</sup>.

Superacids such as  $\text{FSO}_3\text{H-SbF}_5$  act as very effective hydrogen abstracting agents, allowing the generation of carbocations from saturated hydrocarbons <sup>47</sup>.



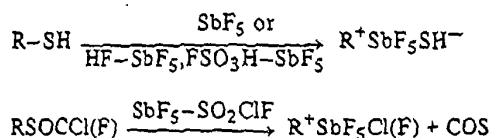
Alkyl cations can also be generated by decarbonylation of tertiary acylium ions, like the Pivaloyl cation *15* <sup>27</sup>.



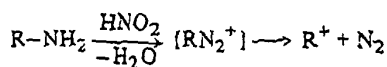
## The Search of Stable Carbocations

This reaction corresponds to the reverse of the Koch-Haaf acid synthesis, which is known to involve carbocation intermediates. Indeed the reaction of the tertiary butyl cation with carbon monoxide gives the pivaloyl cation<sup>27, 48</sup>.

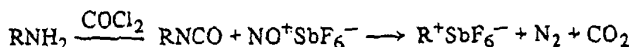
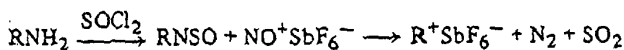
Thiols and thioesters (sulfides) can also be used, similarly to their oxygen analogs, as precursors for alkyl cations<sup>49</sup>. Ionization with  $\text{SbF}_5$  type superacids generally necessitates somewhat more forcing conditions (higher temperatures). Alkyl thiolhaloformates also form alkyl cations via fragmentative ionization<sup>50</sup>.



Amines also can be used as precursors for the generation of alkyl cations. The classic method of deaminative formation of carbocations involves some type of diazotization reaction producing an equimolar amount of water.



Newer methods overcome this difficulty. The corresponding sulfinylamine or isocyanate is prepared and then reacted with stable nitrosonium salts to give the corresponding carbocation<sup>51</sup>.



*h. Observation in Different Superacids.* Whereas antimony pentafluoride containing superacids (such as  $\text{HF-SbF}_5$ ,  $\text{FSO}_3\text{H-SbF}_5$ ,  $\text{CF}_3\text{SO}_3\text{H-SbF}_5$ , etc.) are the preferred solvents for obtaining alkylcations, other superacids such as  $\text{HF-BF}_3$ ,  $\text{HF-TaF}_5$ , etc. can also be on occasions used successfully. The stability of carbocations in these solvents is generally somewhat lower.

## 6. Cyclopropylmethyl Cations

Solvolysis studies of Roberts<sup>52</sup> and Hart<sup>53</sup> showed both the unusual stability of cyclopropylmethyl cations and the ease with which such ions rearrange. Cyclopropyl groups have a strong stabilizing effect on neighboring carbocation center by delocalizing charge through bent  $\sigma$ -bonds. The direct observation<sup>54</sup> of a variety of cyclopropylmethyl cations in cyclic, acyclic and polycyclic systems by NMR spectroscopy provides one of the clearest examples of delocalization of positive charge into a saturated system.

The first cyclopropylmethyl cation directly observed was the tricyclopropylmethyl cation 16 by Deno<sup>54</sup>. Its  $^1\text{H}$  NMR spectrum in  $\text{H}_2\text{SO}_4$  consists of a single sharp line at  $\delta$  2.26. In the 300 MHz  $^1\text{H}$  NMR spectrum in  $\text{SO}_2\text{ClF/SbF}_5$  solution,

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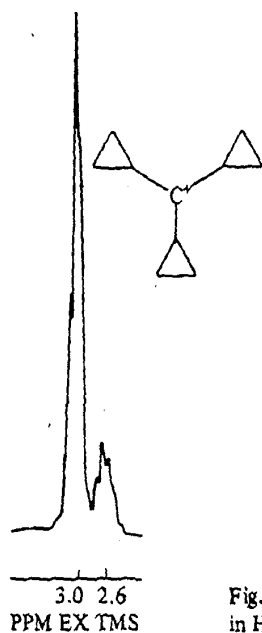


Fig. 4.  $^1\text{H}$ -NMR spectrum (300 MHz) of the tricyclopropylcarbenium ion in  $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2\text{ClF}$  at  $-60^\circ$

however, the methine and methylene protons are well resolved<sup>55)</sup> (Fig. 4). Since then a wide variety of cyclopropylmethyl cations have been prepared and studied by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy<sup>56, 57)</sup>. These studies have lead to the conclusion that cyclopropylmethyl cations adopt bisected geometry and are static in nature with varying charge delocalization into the cyclopropane ring. Most interesting of these ions is the dimethylcyclopropylmethyl cation 17 (Fig. 5). The methyl groups

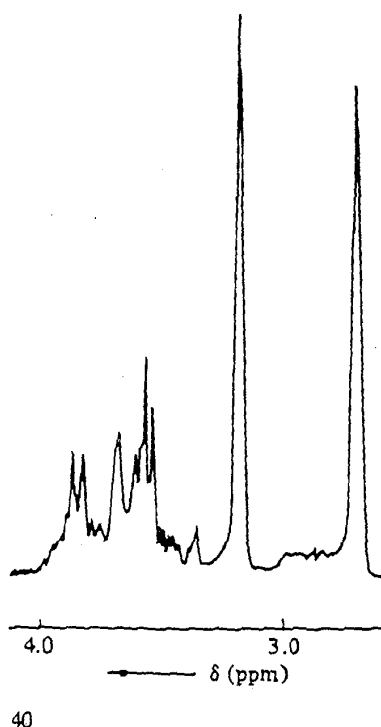
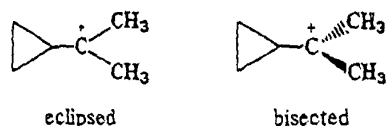


Fig. 5. 100-MHz  $^1\text{H}$ -NMR spectrum of the dimethylcyclopropylcarbenium ion (14)

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are non-equivalent and show a shift difference of 0.54 ppm. The energy difference between bisected and eclipsed structures<sup>17)</sup> is estimated to be 13.7 kcal/mole<sup>58)</sup> (by temperature dependent NMR studies) and is quite close to 12.3 kcal/mole energy obtained by molecular orbital calculations at the minimal basis set STO - 3G level<sup>59)</sup>.



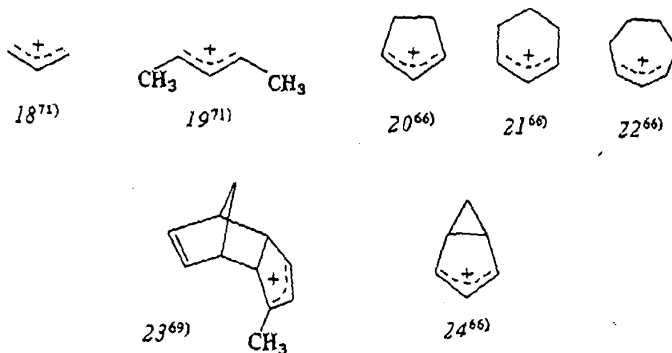
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A wide range of studies<sup>55, 60-62)</sup> have indicated that a cyclopropyl group is equal or more effective than a phenyl group in stabilizing an adjacent carbocation center.

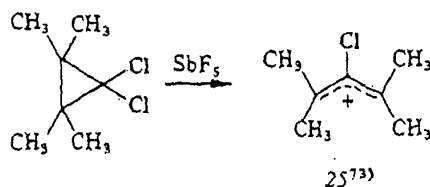
In contrast to "classical" tertiary and secondary cyclopropylmethyl cations (showing substantial charge delocalization into the cyclopropane ring but maintaining its identity) primary cyclopropylmethyl cations in contrast show completely  $\sigma$ -delocalized non-classical carbonium ion character (see subsequent discussion).

## 7. Alkenyl Cations

Many alkenyl cations have now been directly observed particularly by Deno and Richey<sup>24, 63)</sup>, Sorenson<sup>64)</sup>, Olah<sup>65-69)</sup>, and Carpenter<sup>70)</sup>. Deno has reviewed the chemistry of these ions<sup>71)</sup>. Allylic cations particularly show great stability with generally insignificant 1,3-overlap, exempt of cyclobutenyl cations<sup>72)</sup>. Representative observed alkenyl cations are:

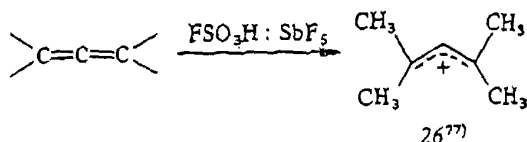


The formation of allyl cations from halocyclopropanes via ring opening of the unstable cyclopropyl cations has been also investigated<sup>73-76)</sup>.



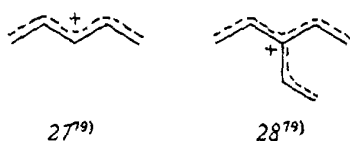
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Protonation of allenes also leads to allyl cations, allowing to obtain ions which are otherwise difficult to obtain from allylic precursors<sup>77-78</sup>.

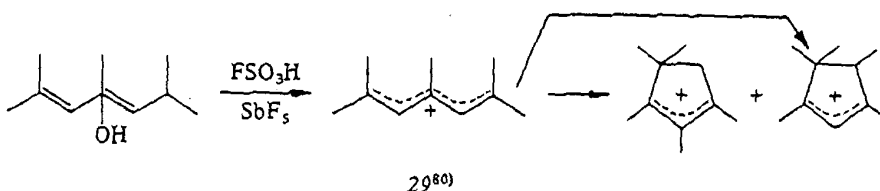


### 8. Alkadienyl and Polyenylic Cations

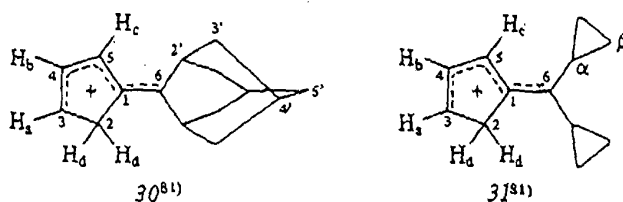
Deno, Richey and their co-workers<sup>24</sup>) have observed a substantial number of alkadienyl cations. Sorensen<sup>79</sup>) has observed divinyl and trivinyl cations 27 and 28.



Alkadienyl cations show great tendency to cyclize and these reactions have been followed by NMR<sup>80</sup>). More recently several novel fulvenes have been protonated to



their corresponding dienylcations<sup>81</sup>) (30, 31, etc.)



### 9. Arenium Ions

Cycloalkadienyl cations, particularly cyclohexadienyl cations (benzenium ions) the intermediate of electrophilic aromatic substitution frequently show remarkable stability. Protonated arenes can be readily obtained from aromatic hydrocarbons with strong acids<sup>82-84</sup>) and advantageously studied by  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectroscopy<sup>85, 86</sup>). Olah et al. even prepared and studied the parent benzenium ion  $\text{C}_6\text{H}_7^+$ <sup>86</sup>). Representative PMR spectra of benzenium ion<sup>86</sup>) 34 and naphthalenium ion<sup>88</sup>) 35 are shown in Figs. 6 and 7. Anthracenium ions<sup>89</sup>) as well as the isomeric



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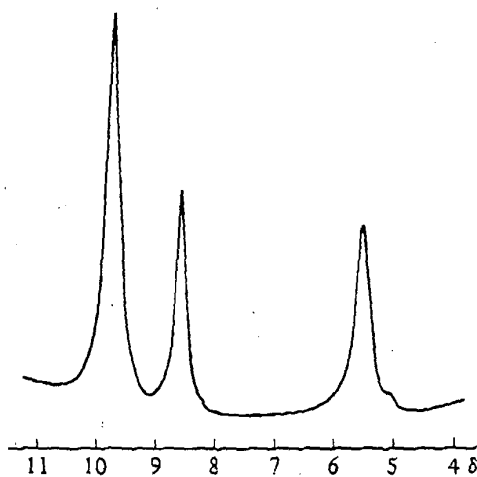


Fig. 6. The 270-MHz FT  $^1\text{H}$ -NMR spectrum of the "static" benzenium ion in  $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2\text{ClF-SO}_2\text{F}_2$  solution at  $-140^\circ\text{C}$

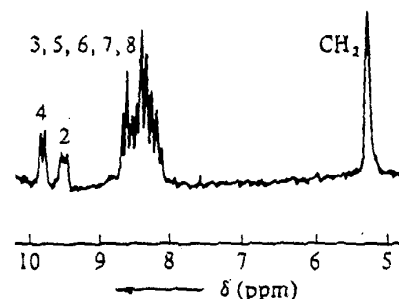


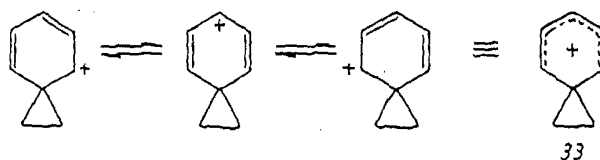
Fig. 7. 100-MHz  $^1\text{H}$ -NMR spectrum of the naphthalenium ion (31) at  $-90^\circ\text{C}$

mono-, di-, tri-, tetra- and pentaalkylbenzenium and halobenzenium ions have been observed<sup>88-89</sup>). Alkylation, nitration, halogenation etc. of hexamethylbenzene gives the related ions. Doering and Saunders prepared the very stable heptamethylbenzenium ion<sup>87</sup>) 32.

### Ethylenarenium Ions

The classical-nonclassical ion controversy also frequently included the question of the so-called "ethylenephonium" ions.

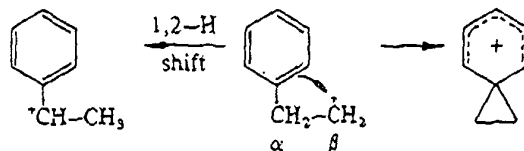
Cram's original studies<sup>90</sup>) established, based on kinetic and stereochemical evidence, the nonclassical bridged ion nature of  $\beta$ -phenylethyl cations in solvolytic systems. Spectroscopic studies (particularly PMR and CMR<sup>91a</sup>) of a series of stable long-lived ions proved the symmetrically bridged structure, and at the same time showed that these ions do *not* contain a pentacoordinated carbocation center (thus are not "nonclassical ions"). They are spiro (2,5)-octadienyl cations (spirocyclopropylbenzenium ions), in other words cyclopropylmethyl cations in which the carbocation center belongs to a cyclohexadienyl cation (benzenium ion).



The nature of the spiro carbon atom is of particular importance in defining the carbocation nature of the ions. CMR spectroscopic studies clearly established the aliphatic tetrahedral nature of this carbon, thus ruling out a "nonclassical" pentacoordinated carbocation.

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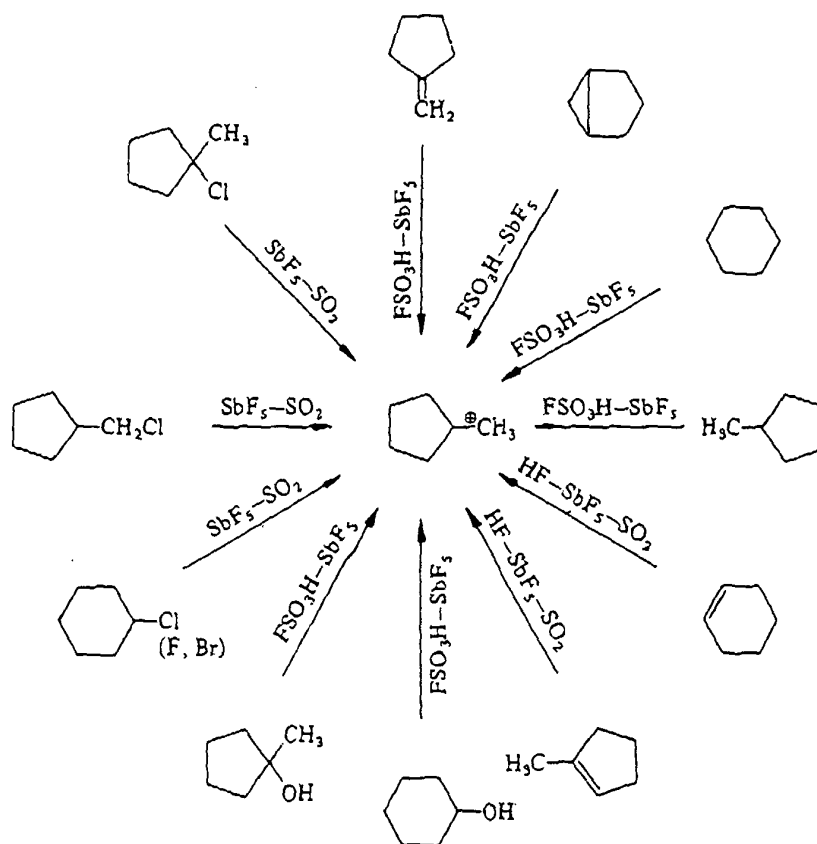
The formation of the ethylenebenzenium ion **33** from  $\beta$ -phenylethyl precursors can be depicted as cyclization of the aromatic  $\pi$ -systems and not of the  $C_{AR}-C_{\alpha}$



bond which would give the tetracoordinated ethylenephonium ion. Rearrangement of the  $\beta$ -phenylethyl to  $\alpha$ -phenylethyl (styryl ions) on the other hand takes place through a regular 1,2-hydrogen shift. Rearrangement and equilibria of ions formed from side chain substituted  $\beta$ -phenylethylchlorides have also been explored<sup>91d</sup>.

#### 10. Cycloalkyl Cations

Tertiary cycloalkylations, such as the 1-methyl-1-cyclopentyl cation **36** show high stability in strong acid solutions. This ion can be obtained from a variety of precursors<sup>92</sup> (Fig. 8).



## The Search of Stable Carbocations

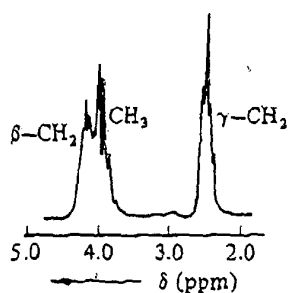
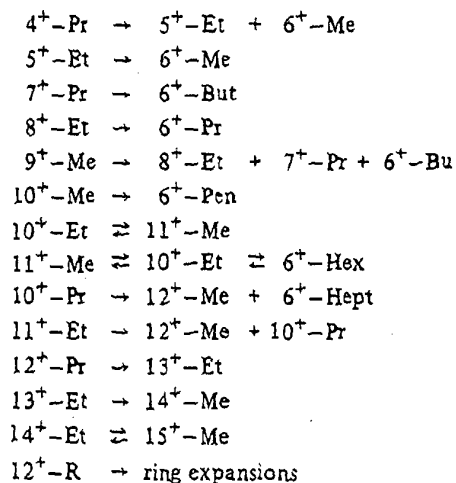


Fig. 8. 60-MHz  $^1\text{H}$ -NMR spectrum of the 1-methyl-1-cyclopentyl cation at  $-60^\circ\text{C}$

It is worthwhile to mention that not only cyclopentyl but also the cyclohexyl type precursors gives the 1-methylcyclopentyl cation 36. This indicates that the cyclopentyl cation has higher stability, which causes isomerization of the secondary cyclohexyl cation to the tertiary methylcyclopentyl ion.

The cyclopentyl cation 37 shows in its proton magnetic resonance spectrum in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution, even at  $-150^\circ$ , only a single absorption line at  $\delta$  4.68<sup>40, 90</sup>. This observation indicates a completely degenerate ion with a low barrier to the secondary-secondary hydride shift (see subsequent discussion). Sorensen et al.<sup>93</sup> have prepared a variety of tertiary cycloalkyl cations of different ring sizes  $n = 4$  (small ring),  $n = 5-7$  (common rings),  $n = 8-11$  (medium rings), and  $n = 12-20$  (large rings). These ions were in general found to undergo ring expansion or contraction reactions, often in multiple or repetitive steps, as shown in the following sequence.



The parent secondary cyclobutyl cation 38 undergoes immediate rearrangement via  $\sigma$ -bond delocalization into the equilibrating non-classical bicyclobutonium ion like system<sup>94, 95</sup> (see subsequent discussion of non-classical ions). Similar behaviour is also observed for the 1-methylcyclobutyl cation<sup>94, 94-98</sup> 39. The 1-phenylcyclobutyl cation 40 on the other hand is a classical tertiary carbocation<sup>94</sup>.

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## 11. Bridgehead Carbocations

Bredt's rule in its original form<sup>99</sup> excluded the possibility of carbocation formation at bridgehead positions of cycloalkanes. Indeed, bridgehead halides, such as apocamphylchloride, proved extremely unreactive under hydrolysis conditions<sup>100</sup>. However, 1-bromoadamantane very readily gives the bridgehead carboxylic acid under the usual conditions of Koch-Haaf acid synthesis<sup>101</sup>. 1-Fluoroadamantane is ionized in  $\text{SbF}_5$  to give the stable bridgehead adamantyl cation 41<sup>102, 103</sup>.

The PMR spectrum of the adamantyl cation in  $\text{SbF}_5$  solution at 25 ° consists of resonances at  $\delta$  5.40,  $\delta$  4.52 and  $\delta$  2.67 with peak areas of 3:6:6 (Fig. 9). The CMR spectrum (Fig. 9b) shows the  $\gamma$ -carbons more deshielded than the  $\beta$ -s, indicating strong C—C bond hyperconjugation with the empty p-orbital.

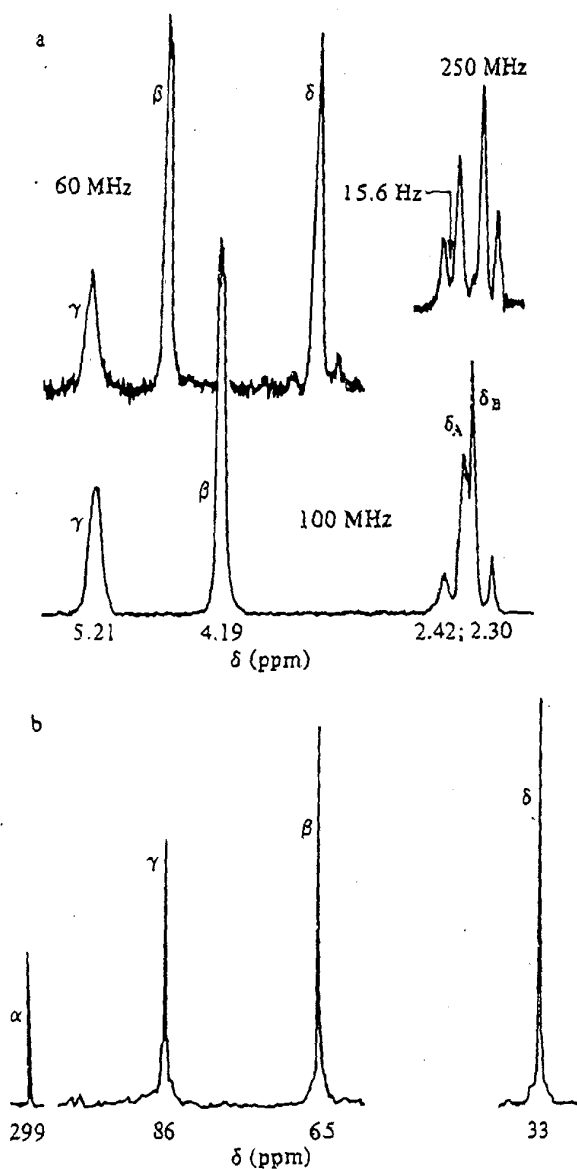
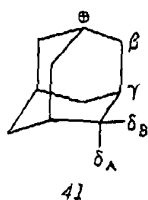
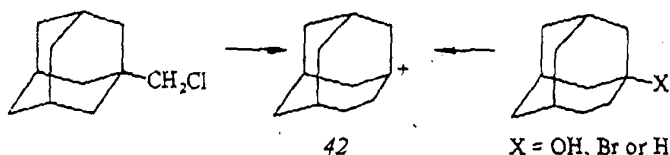


Fig. 9. a)  $^1\text{H}$ -NMR spectrum of the 1-adamantyl cation at 60 MHz, 100 MHz, and 250 MHz; b) Fourier-transform  $^{13}\text{C}$ -NMR of the 1-adamantyl cation (in  $\text{FSO}_3\text{H}-\text{SbF}_5$ )

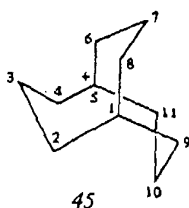
## The Search of Stable Carbocations



Methyl substituted adamantyl cations have also been studied<sup>103</sup>. The bridgehead homoadamantyl cation 42 has been obtained<sup>104</sup> from both adamantylcarbinyll and homoadamantyl precursors. Bridgehead bicyclo [4.4.0] decyl, bicyclo [4.3.0] nonyl



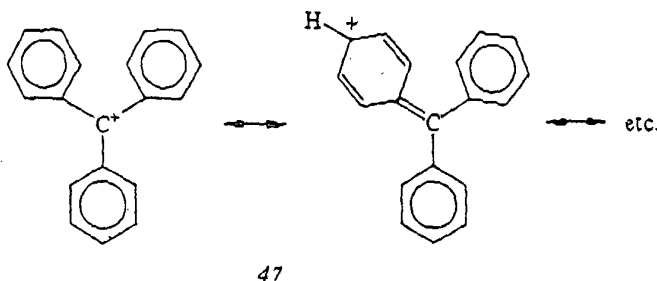
and bicyclo [3.3.0] octyl cations 43, 44, and 45 are found to be equilibrating ions<sup>105</sup>. More recently bridgehead bicyclo [3.3.3] nonyl cation 46 has been prepared and studied<sup>106</sup> by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.



The bridgehead congressane (diamantane) cation 46 has also been observed<sup>103</sup>. Although the bridgehead 1-norbornyl cation was not directly observed, 1-chloro-norbornane yields the stable 2-norbornyl cation in SbF<sub>5</sub>-SO<sub>2</sub> solution<sup>107</sup>. Thus, ionization to the bridgehead carbonium ion must be followed by a fast shift of hydrogen from C-1 to C-2, the driving force for which is obviously the tendency to relieve strain in the carbenium ion.

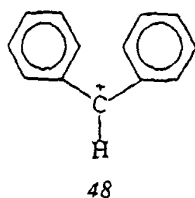
## 12. Aryl- and Alkylaryl methyl Cations

The first stable long-lived carbocation observed was the triphenylmethyl cation<sup>108-110</sup> 47.

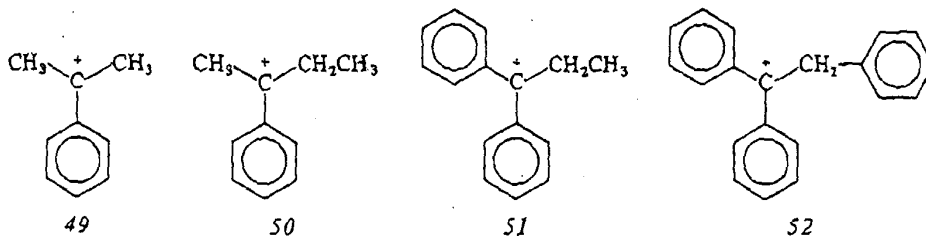


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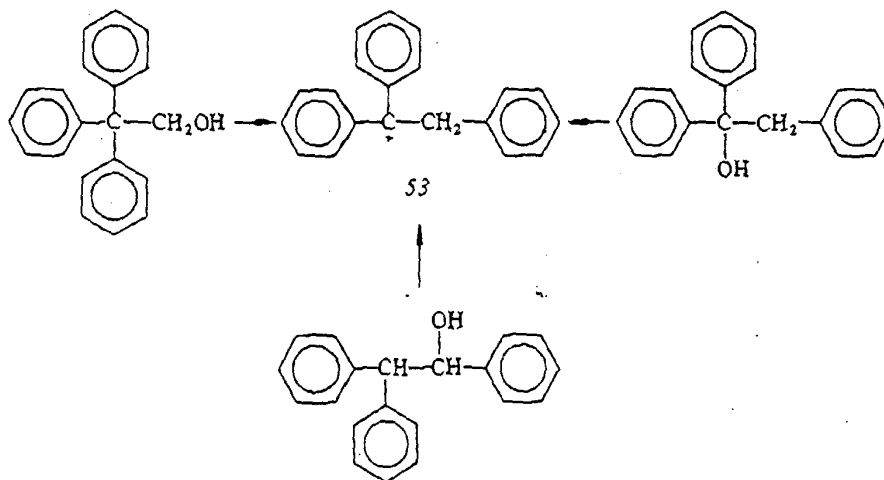
This ion is still the best-investigated carbocation<sup>2)</sup> and its propeller-shaped structure is well proved. Strong contribution from para (and ortho) quinonoidal resonance forms in the ion make it probable that these reactive secondary forms are responsible for much of the reactivity of the ion. Diphenylmethyl cations (benzhydryl cations) are considerably less stable than their tertiary analogs. Although ultraviolet spectra in dilute sulfuric acid solutions have been obtained<sup>111)</sup>, only recently has the benzhydryl ion 48 been observed in higher concentrations in acid solutions [ $\text{ClSO}_3\text{H}$ <sup>112)</sup>,  $\text{FSO}_3\text{H}$ <sup>113)</sup>, and  $\text{FSO}_3\text{H}-\text{SbF}_5$ ]<sup>114)</sup>.



Mono- and dialkylarylmethyl cations can be readily obtained from the corresponding alcohols, olefins, or halides in strong acid solution, such as  $\text{H}_2\text{SO}_4$ <sup>111)</sup>,  $\text{FSO}_3\text{H}-\text{SbF}_5$ <sup>114)</sup>,  $\text{ClSO}_3\text{H}$  and  $\text{FSO}_3\text{H}$ <sup>112)</sup>, and oleum<sup>113)</sup>. Representative alkylarylmethyl cations are:



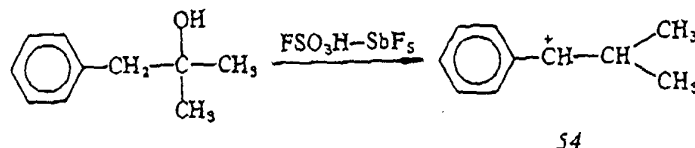
Because of the high stability of the tertiary ions, these are preferentially formed in the strong acid systems from both tertiary, secondary, and even primary precursors<sup>115)</sup>.



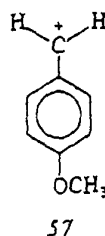
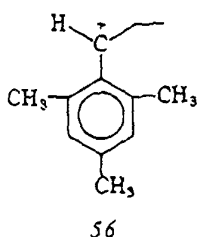
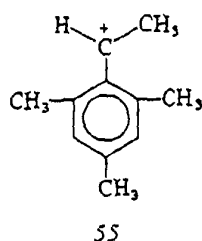
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## The Search of Stable Carbocations

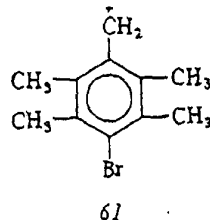
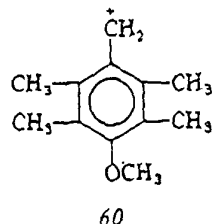
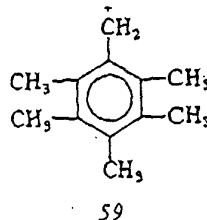
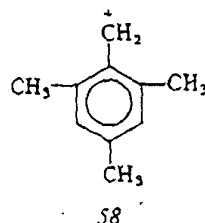
If, however, the tertiary carbocation is not benzylic, rearrangement to a secondary, benzylic ion can be observed:



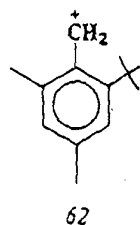
With suitable substituent groups (which also prevent transalkylations) secondary styryl cations were found as stable, long-lived ions<sup>116, 117</sup>.



Although the unsubstituted benzyl cation is still elusive, many substituted derivatives have been observed<sup>116</sup>.



In a cation such as the (2,4-dimethyl-6-*t*-butyl) benzyl cation 62 a high rotational barrier around  $sp^2$ -hybridized carbon atom is observed. The methylene protons are found magnetically non-equivalent in the  $^1\text{H}$  NMR spectrum<sup>118</sup>.

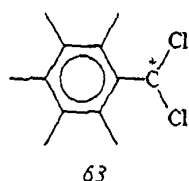


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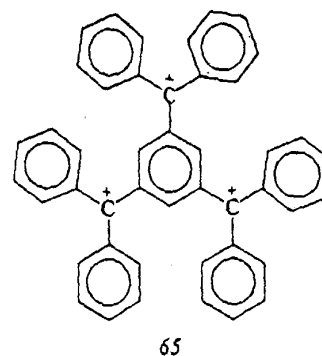
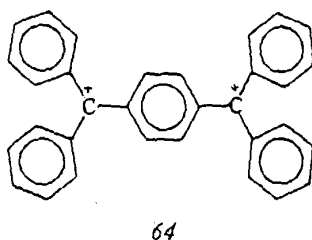
No rearrangement of benzyl cations in acid solution to tropylium ions has been found, although this rearrangement is claimed in the gas phase (mass spectroscopy).

## 13. Carbocations

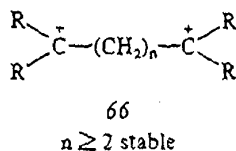
Early reports<sup>119)</sup> that a carbocation had been observed from pentamethyltrichloromethyl benzene turned out to be incorrect. The species obtained was the dichloropentamethylbenzyl cation **63**<sup>120-122)</sup>.



If two carbocation centers are separated by a phenyl ring, a variety of carbodi- and tri-cations can be obtained<sup>123, 124)</sup>.



Separation of the two carbocation centers by at least two methylene groups in open chain carbocations also enables these ions to be obtained as stable species in superacidic systems<sup>125)</sup>.



A comprehensive NMR spectroscopic study<sup>126)</sup>, of a series of acyclic carbocations was carried out. Carbocations were also observed in more rigid systems, such as the apical, apical congressane dication **67**<sup>103)</sup>, bicyclo [2.2.2] octyl dication **68**<sup>127)</sup> and bicyclo [3.3.3] nonyl dication **69**<sup>106)</sup> (manxyl dication - Fig. 10).

Many aromatic stabilized dications have been prepared and characterized by NMR spectroscopy (see subsequent discussion).



## The Search of Stable Carbocations

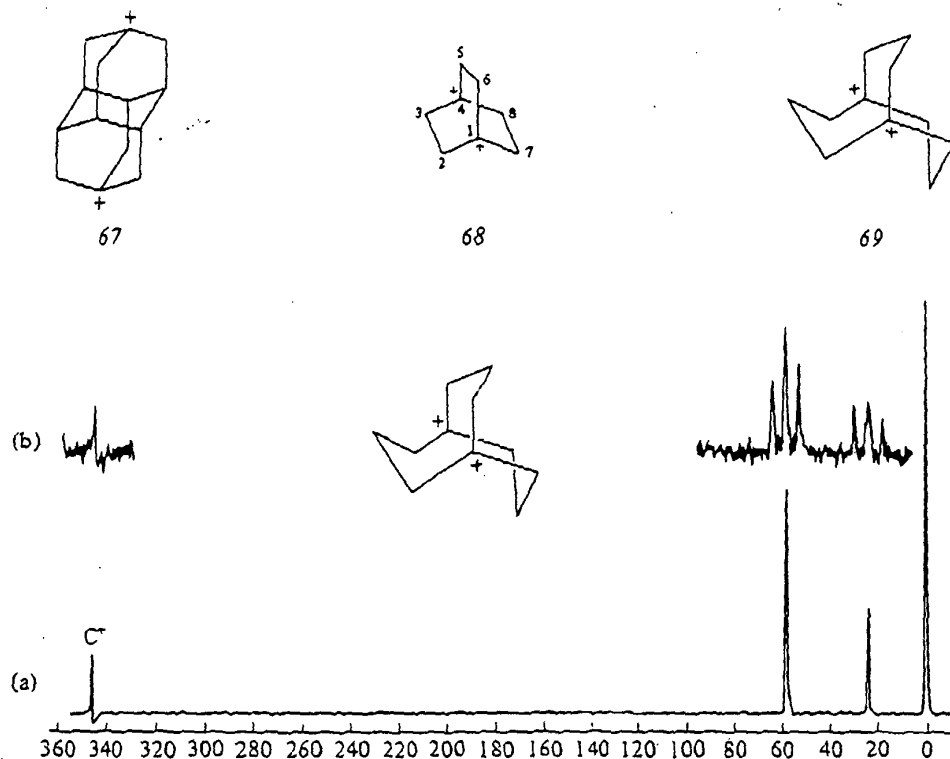
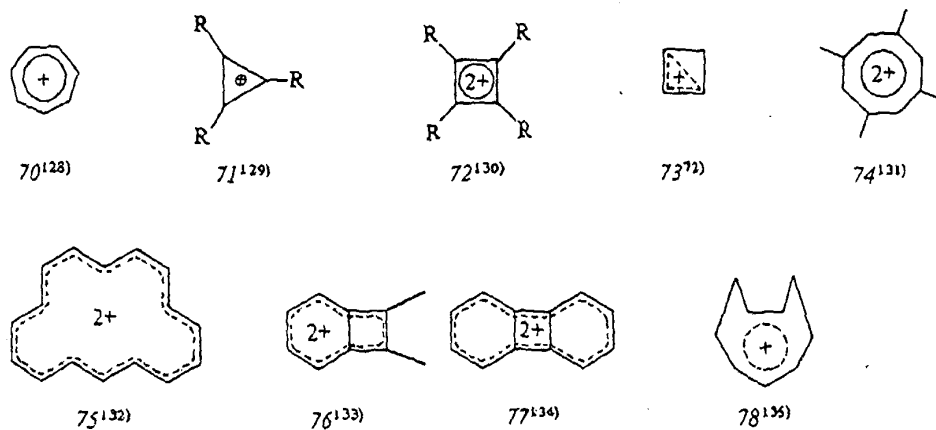


Fig. 10A. The 25 MHz  $^{13}\text{C}$ -NMR spectrum of the bicyclo[3.3.3]nonyldication 69 in  $\text{SbF}_5\text{SO}_2\text{ClF}$  solution

## 14. Aromatically Stabilized Carbocations

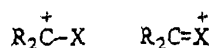
If a carbocation at the same time is also a Huckeloid ( $4n+2$ )  $\pi$  aromatic system, resonance can cause substantial stabilization. There were numerous aromatically stabilized Huckeloid systems<sup>128-135</sup> generated in superacidic media in recent years and characterized by NMR spectroscopy. Some of the best known examples are the following.



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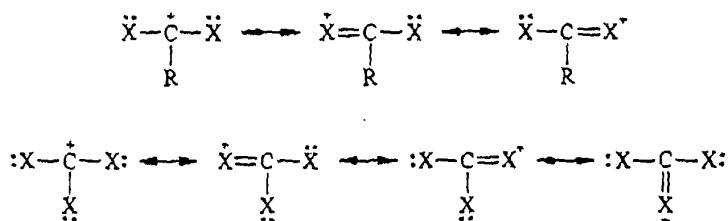
## 15. Heteroatom-Stabilized Carbocations

In contrast to hydrocarbon cations, heteroatom-substituted carbocations are strongly stabilized by electron donation from the unshared electron pairs of the heteroatoms adjacent to the carbocation center:



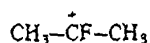
$X = Br$  or  $NR_2$ ,  $SR$ ,  $F$ ,  $Cl$

The stabilizing effect is enhanced when two, or even three, electron-donating heteroatoms coordinate with the electron-deficient carbon atom.

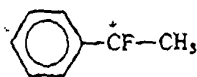


## 16. Halogen as Heteroatom

In 1965 with Comisarow and Cupas we reported the first fluoromethyl cation<sup>136</sup>. Since then a large variety of fluorine substituted carbocations have been prepared. Fluorine has a particular ability to stabilize carbocations via back coordination of its unshared electron pairs into the vacant p orbital of the carbocationic carbon atom.<sup>137</sup> <sup>19</sup>F NMR spectroscopy is a particularly efficient tool for the structural investigations of these ions<sup>137</sup>. The 2-fluoro-2-propyl and 1-phenylfluoroethyl cations 79 and 80 are representative examples of the many reported similar ions<sup>138</sup>.



79



80

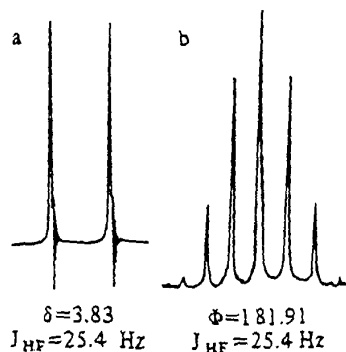
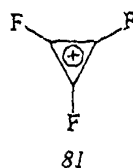


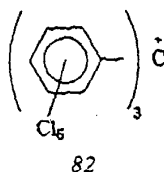
Fig. 10B. a) <sup>1</sup>H-NMR spectrum of the dimethylfluorocarbenium ion at 60 MHz:  $J_{HF} = 25.4$  Hz; b) <sup>19</sup>F-NMR spectrum of the same ion at 56.4 MHz:  $J_{HF} = 25.4$  Hz

## The Search of Stable Carbocations

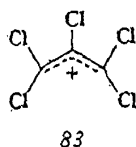
Trifluoromethyl<sup>139)</sup> and perfluorophenyl substituted carbocations have also been prepared and studied<sup>140, 141)</sup>. Because of the relatively large fluorine chemical shifts, anisotropy and ring current effect play a relatively much smaller role than they do in the case of proton shifts. Therefore, a better correlation of charge distribution with chemical shifts can be obtained. The trifluorocyclopropenium ion **81** was also reported<sup>142)</sup>.



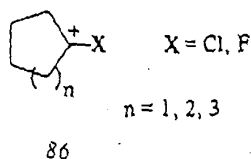
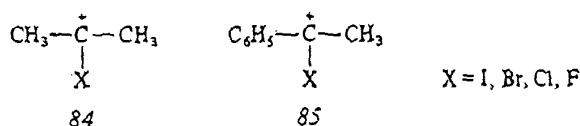
A series of chloromethyl cations were observed, including phenyldichloromethyl cations<sup>120-122, 143)</sup>, and perchlorotriphenylmethyl ion **82**<sup>144)</sup>.



West has characterized the perchloroallyl cation **83**. A series of chloro-, as well as



bromo- and iodomethyl cations have been observed and the general stabilizing effect of halogen attached to carbocation center has been demonstrated<sup>146)</sup>. With Halpern and Mo we were able to study these effects in detail using <sup>13</sup>C NMR spectroscopy<sup>147)</sup>.



Three and five-membered ring halonium ions were obtained in our work with Bollinger<sup>148)</sup> and studied with Peterson<sup>149)</sup>. Illustrative is the propylenebromonium ion whose PMR spectrum is shown in Fig. 11.

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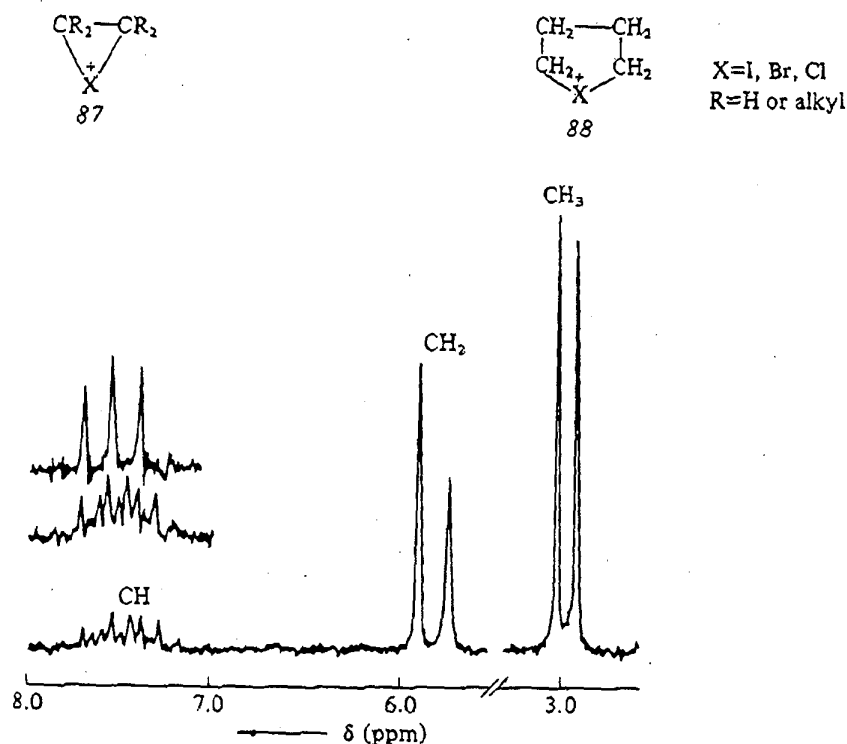
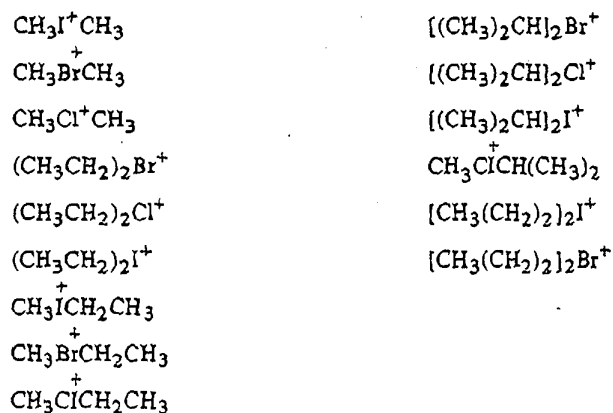


Fig. 11. <sup>1</sup>H-NMR spectrum (at 60 MHz) of the propylenebromonium ion; Left: signal of methine protons decoupled

Not only ring halonium ions, but also a series of open chain dialkylhalonium ions were obtained in our work with DeMember<sup>150</sup>, such as the following

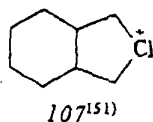
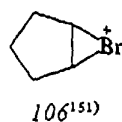


90-105

Dialkylhalonium fluoroantimonate salts can be isolated as crystalline salts and are versatile, very reactive alkylating agents. As the differing halogen atoms effect a range of selectivity, they were found to be more versatile than trialkyloxonium salts.

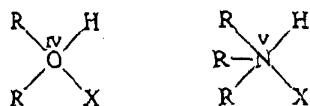
Several bicyclic halonium ions also have been prepared and studied<sup>151</sup>.

## The Search of Stable Carbocations

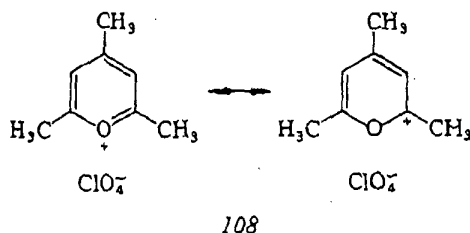


## 17. Oxygen as Heteroatom

Crystalline addition compounds of alcohols, ethers, aldehydes, and ketones with Brønsted and Lewis acids have been known since the middle of the last century. They were long considered unstable "molecular compounds"<sup>152</sup>. Collie and Tickle<sup>153</sup> were the first to assign "oxonium salt" character to the acid complexes as containing a tetravalent oxygen, analogous to the ammonium salts in which nitrogen at that time was assumed to be pentavalent:

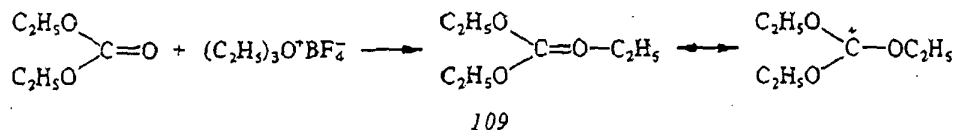


The ionic structure of the pyrylium salts were clearly stated by Hantzsch as early as 1922<sup>154</sup>.

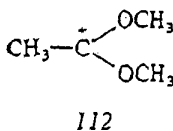
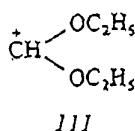
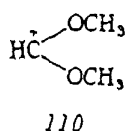


In pyrylium salts there is contribution from carbocation structures, a fact apparent in the behavior toward strong nucleophiles leading to phenols.

a) *Alkoxy- and Hydroxylated Carbocations*: Resonance, similar to that in pyrylium salts was shown<sup>155</sup> to exist between tri- and dialkyloxonium and carboxonium ion forms in alkylated ketones, esters and lactones which were obtained via trimethyl or triethyloxonium fluoroborates.

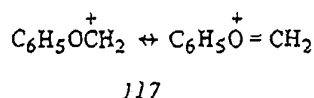
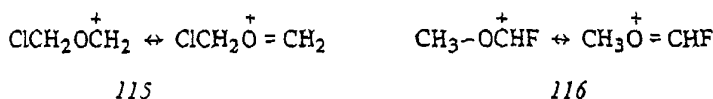


Taft and Ramsey<sup>156</sup> used <sup>1</sup>H NMR spectroscopy to investigate the nature of a series of secondary and tertiary carboxonium ions.

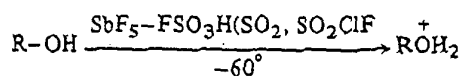


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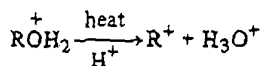
With Bollinger<sup>157)</sup> we obtained primary carboxonium ions such as methoxy- and phenoxymethyl cations and their halogenated derivatives



Acidic oxonium ions can be readily obtained and studied in superacidic media. With Sommer and Namanworth<sup>43)</sup> we showed that primary and secondary alcohols are protonated in  $\text{FSO}_3\text{H-SbF}_5(\text{SO}_2, \text{SO}_2\text{ClF})$  solution at  $-60^\circ$ , giving well-resolved spectra of the alkyloxonium ions.

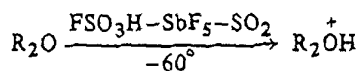


At higher temperature they cleave to alkyl cations; the kinetics of these cleavage reactions could be followed by NMR spectroscopy.

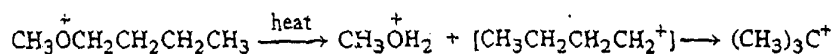


Tertiary alcohols (with the exception of the ones containing strong electron withdrawing groups, such as  $\text{CF}_3$ ) generally dehydrate very fast in the acid media, and the intermediate protonated species cannot be observed, even at low temperatures before cleavage.

Ethers also protonate in superacid media<sup>45)</sup> to give dialkyloxonium ions.

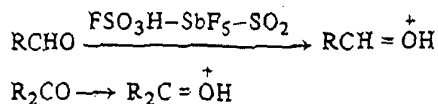


Again cleavage reactions can be followed by NMR spectroscopy as in the case of methyl *n*-butyl ether



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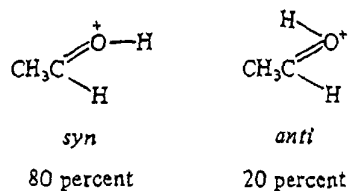
Aldehydes and ketones protonate on the carbonyl oxygen atom, and in superacid media at low temperatures to the corresponding carboxonium ions which can be directly observed<sup>158-162)</sup>



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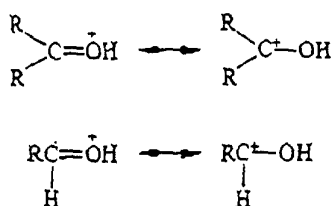
## The Search of Stable Carbocations

Even protonated formaldehyde was observed. Protonated acetaldehyde was observed in two isomeric forms, the proton on oxygen being *syn* or *anti* to the methine proton:

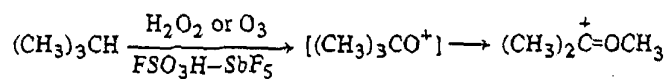


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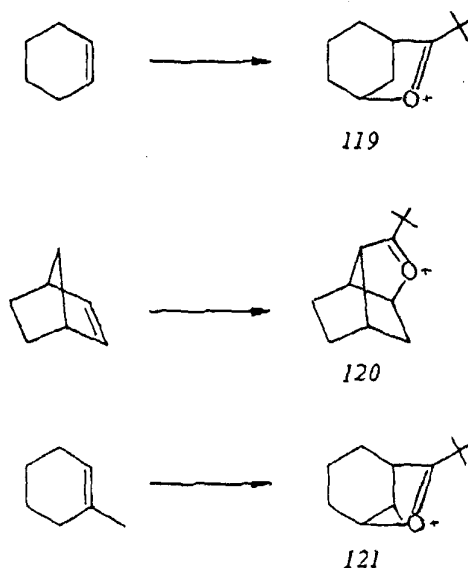
The hydroxymethyl cation forms of protonated ketones and aldehydes contribute to the resonance hybrid. Based on  $^{13}\text{C}$  NMR studies<sup>162, 163a</sup>, the degree of contribution of the hydroxymethyl cation forms can be quite accurately estimated.



Alkylated carboxonium ions have also been prepared by direct electrophilic oxygenations of alkanes, alcohols, etc. by ozone or hydrogen peroxide in superacidic media<sup>164</sup>.

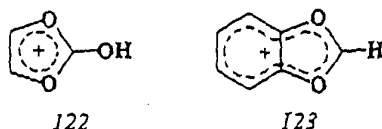


Smith et al. have isolated a series of cyclic carboxonium salts (such as 119–121) by acylation of alkenes.



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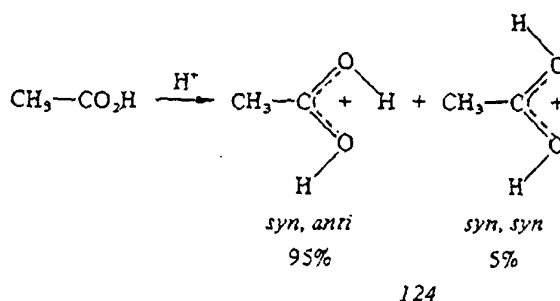
$^{13}\text{C}$  NMR spectral investigations have been extended<sup>163b)</sup> to the study of hetero-aromatic stabilized 6  $\pi$ ,3-dioxolium and 10  $\pi$  benzo-1,3-dioxolium ions 122 and 123.



Carboxylic acids are protonated in superacid media, such as  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ ,  $\text{HF}-\text{SbF}_5$ , or  $\text{HF}-\text{BF}_3$ <sup>166)</sup>. The NMR spectrum of acetic acid in such media at low temperature shows two OH resonances indicating

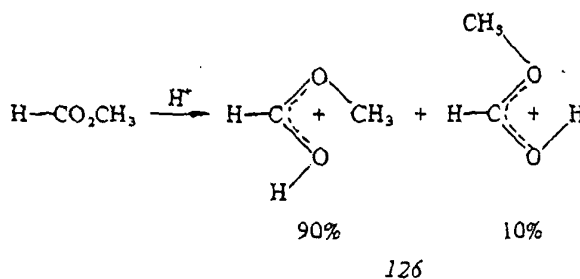
- (i) that carbonyl protonation is favored and
- (ii) that hindered rotation about the resultant COH bonds is present.

The predominant conformer observed is the *syn, anti*, although about 5 percent of the *syn, syn* isomer has also been seen.



These isomers can be readily identified from the magnitudes of the vicinal coupling constants; thus in the *syn, anti* isomer, the methine proton is a doublet of doublets ( $J_{\text{HH}} = 15$  and 3.5 hertz) while in *syn, syn* isomer a triplet is observed ( $J_{\text{HH}} = 3.5$  hertz). No evidence for the *anti, anti* isomer has been found in either protonated carboxylic acids, esters, or their analogs.

Esters behave in an analogous fashion, with carbonyl protonation being predominant. Thus protonated methyl formate is present in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$  solution as two isomers in a ratio of 90% to 10%<sup>167)</sup>.



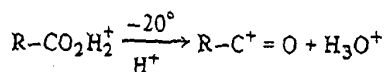
By raising the temperature of solutions of protonated carboxylic acids and esters, unimolecular cleavage reactions are observed. These reactions can be considered within the framework of the two unimolecular reaction pathways for acid-



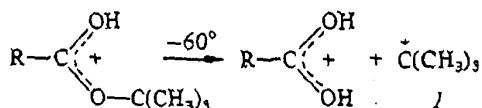
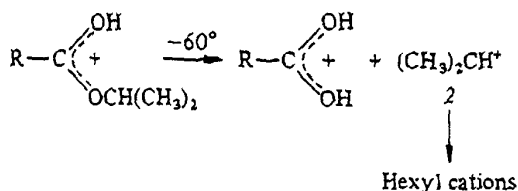
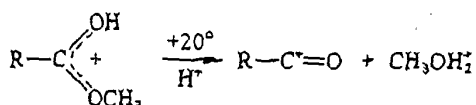
## The Search of Stable Carbocations

catalyzed hydrolyses of esters, either involving alkyl- or alkyl-oxygen cleavage. The advantage of studies of these reactions in superacid media, as compared to solvolytic conditions, is that the cleavage step can be isolated and studied in detail because the cleavage products generally do not undergo any further reaction.

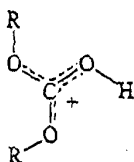
For example, in the case of protonated acetic acid in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$  solution, a reaction analogous to the rate-determining step in the unimolecular cleavage of esters is observed leading to the acyl cation and oxonium (hydronium) ion.



Unimolecular cleavage in this case, corresponds to dehydration of the acid, but in the case of protonated esters the cleavage pathway depends on the nature of the alkoxy group.

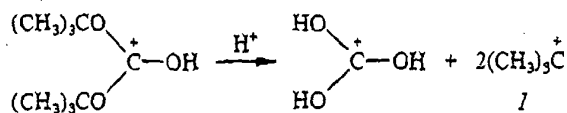


Dialkyl carbonates have been studied in  $\text{FSO}_3\text{H}-\text{SbF}_5$  solution and have been shown to be protonated on the carbonyl group giving the dialkoxyhydroxy methyl cation<sup>168</sup>.



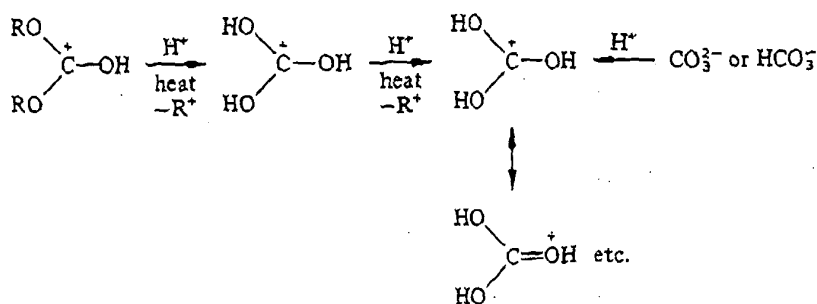
Di-*t*-butyl carbonate cleaves immediately at  $-80^\circ$  with alkyl-oxygen fission, giving the *t*-butyl cation **1** and protonated carbonic acid. The structure of the latter has been established from the  $^{13}\text{C}$  NMR spectrum of the central carbon atom which shows a 4.5 hertz quartet, being coupled to three equivalent hydroxyl protons<sup>168</sup>.

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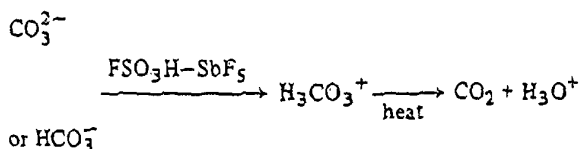
Di-isopropyl and diethyl carbonate cleave at a higher temperature, also via alkyl-oxygen cleavage, with initial formation of protonated alkyl hydrogen carbonates. The alkyl hydrogen carbonates can also be formed by protonation of their sodium salts.



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Protonated carbonic acid can also be obtained by dissolving inorganic carbonates and hydrogen carbonates in  $\text{FSO}_3\text{H}-\text{SbF}_5$  at  $-80^\circ$ . It is stable in solution to about  $0^\circ$ , where it decomposes to the hydronium ion and carbon dioxide.

It is worthwhile to point out the close similarity of protonated carbonic acid (trihydroxymethyl cation) with the guanidinium ion, its triaza-analog. Both are highly resonance stabilized through their onium forms.

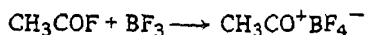


The observation of protonated carbonic acid as a stable chemical entity with substantial resonance stabilization may have also implications in our understanding of some of the more fundamental biological carboxylation processes. Obviously the in vitro observation in specific, highly acidic solvent systems cannot be simply extrapolated to different environments (biological systems). However, it is possible that on the active receptor sites of enzyme systems (for example, those of the carbonic anhydrase type) local hydrogen ion concentration may be very high, as compared with the overall "biological pH." In addition, on the receptor sites a very favorable geometric configuration may help to stabilize the active species, a factor which cannot be reproduced in model systems in vitro.

*b) Acylium Ions (Acyl Carions).* Seel observed in 1943 the first stable acyl cation<sup>16)</sup>. Acetyl fluoride with boron trifluoride gave a complex (decomposition point  $20^\circ$ ) which was characterized as the acetyl tetrafluoroborate salt

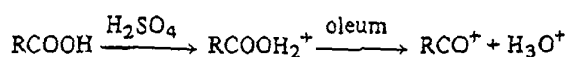
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## The Search of Stable Carbocations

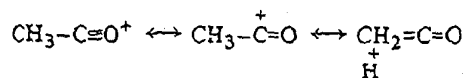


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The identification was based on analytical data and chemical behavior. Only in the 1950's were physical methods like infrared and NMR spectroscopy were applied, making further characterizations of the complex possible. Since 1954, a series of other acyl and substituted acyl cations have been isolated and identified<sup>169-171</sup>. The hexafluoroantimonate and hexafluoroarsenate complexes were found particularly stable<sup>171</sup>. Deno and his co-workers investigated solutions of carboxylic acids in sulfuric acid and oleum<sup>172</sup>. They observed protonation at lower acid concentrations and dehydration, giving acyl cations at higher acidities.



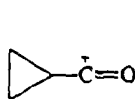
The investigation of acyl cations in subsequent work is substantially helped by NMR. Not only <sup>1</sup>H, but also <sup>2</sup>H, <sup>13</sup>C, and <sup>19</sup>F resonance studies established the structure of these ions<sup>171-174</sup>. These investigations, based on <sup>13</sup>C and proton resonance, showed that acyl cations, such as the  $\text{CH}_3\text{CO}^+$  ion, are not simple oxonium ions (acylonium complexes), but are resonance hybrids of the oxonium ion, acyl cation and the ketene-like non-bonded mesomeric forms



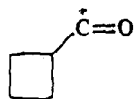
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The X-ray crystallography study of the  $\text{CH}_3\text{CO}^+\text{SbF}_6^-$  complex<sup>175</sup> substantiated this suggestion and provided convincing evidence for the linear structure of the crystalline complex.

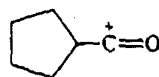
Investigation of acyl cations has been extended to be study of cycloacylium ions<sup>176</sup>, diacylium ions (diacyl cations)<sup>177</sup>, and unsaturated acylium ions<sup>178</sup>.



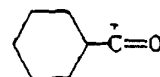
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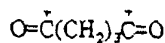
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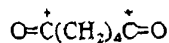
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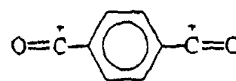
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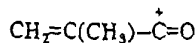
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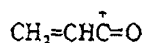
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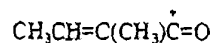
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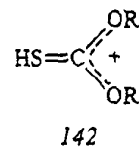
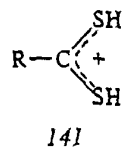
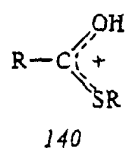
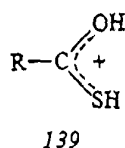
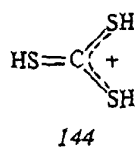
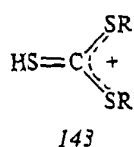


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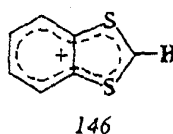
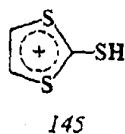
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## 18. Sulfur as Heteroatom

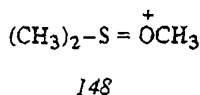
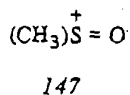
Thiols and sulfides are protonated on sulfur in superacid media and give mono- and dialkylsulfonium ions, respectively<sup>49</sup>. Thiocarboxylic acids, S-alkyl esters, thioesters, dithioesters and thiocarbonates in similar media also form stable protonated ions<sup>179</sup> such as

R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>

sulfur stabilized heteroatomic species such as 145 and 146 are also known<sup>163b</sup>.

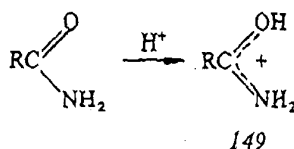


S-methylated and O-methylated dimethyl sulfoxides 147 and 148 have been very extensively studied<sup>180</sup>.



## 19. Nitrogen as Heteroatom

Amides are protonated, in superacid media at low temperatures, on the carbonyl oxygen atom, as shown first by Gillespie<sup>181</sup>.

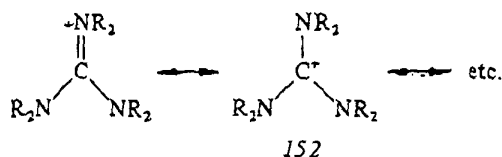
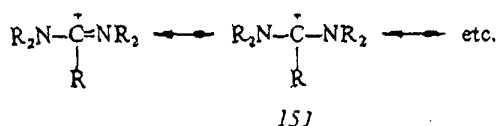
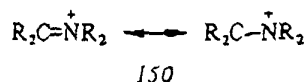


It was claimed that protonation of ethyl N,N-diisopropylcarbamate, a hindered amide, takes place on nitrogen, and not on oxygen<sup>182</sup>. A reinvestigation, however, established, that at low temperature first O-protonation is taking place (kinetic control) with the O-protonated amide subsequently rearranging to the more stable N-protonated form (thermodynamic control)<sup>183</sup>.

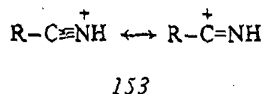
## The Search of Stable Carbocations

The possibility of observing the protonated amide linkage in strong acid media has particular relevance in the study of peptides and proteins<sup>184, 185</sup>.

Since nitrogen is a better electron donor than oxygen, the contribution of aminomethyl cation structures in acid salts of imines, amidines, and guanidines is small<sup>186</sup>.



In protonated nitriles, however, the contribution from the iminomethyl cation resonance form is important<sup>187, 188</sup>.



Recently protonated dialkylnitrosamines have been studied<sup>189</sup> to elucidate alkylating and aminoalkylating ability which due to the carcinogenic activity of nitrosamines is of potential biological significance. Ambident carbocationic nature of iminium ions and its relevance to aminoalkylating ability has also been explored<sup>190</sup>. An in vitro path of nitrosamine formations from amines with nitrates has been demonstrated<sup>191</sup>.

In search of the still elusive nitrenium ions protonation of benzoquinone monoximes was studied<sup>192</sup>. Ions such as the triazomethyl cation have also been reported<sup>193</sup>. The field of protonated heteroaliphatic compounds has been reviewed<sup>178a, 179b</sup>.

### III. Five and Higher Coordinated (Non-Classical) Carbocations

Some carbocations show great tendency to undergo fast degenerate rearrangements, leading through intramolecular hydrogen or alkyl shifts to the related identical structures<sup>2</sup>). The question arises, whether these processes are equilibrations between the limiting trivalent carbocations ("classical ion intermediates") separated by low energy level transition states or whether intermediate hydrogen or alkyl bridged

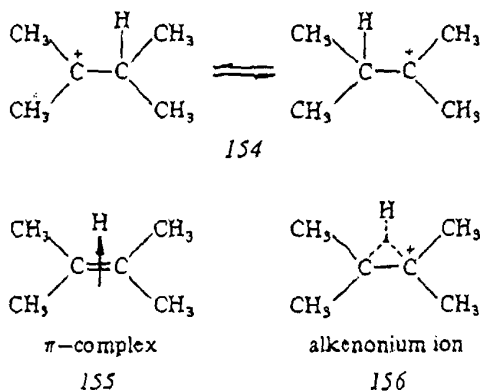
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carbocations are involved. Extensive discussion of the kinetic and stereochemical results in these systems was made and it is not considered part of this review to recapitulate the arguments. The reader is referred to reviews<sup>2)</sup> and the original literature.

As direct observation of long-lived carbocations, in superacidic media, became possible in recent years it was logical to extend the developed spectroscopic and chemical methods to the study of equilibrating and/or bridged carbocations. Differentiation between these possibilities is difficult when using the  $^1\text{H}$  NMR method for the study of these ions. On the slow NMR time scale the proton spectra of rapidly equilibrating or bridged ions can be expected to be quite similar. Carbon-13 NMR spectroscopy can be used, however, advantageously<sup>31, 194)</sup> to investigate the structure of carbocations in which the possibility exists for degenerate rearrangements to occur which are fast with respect to the NMR time-scale and which lead to average shifts and coupling constants.

## 20. Equilibrating Alkyl Cations

An example of rapidly equilibrating alkyl cations is the tetramethylethyl cation 154. It shows a PMR spectrum, in which all four methyl groups are equivalent and thus does not allow a clear distinction to be made between a rapidly equilibrating pair of ions or a static hydrogen bridged ion (which may be formulated either as a  $\pi$ -complex 155 or alkenonium ion 156).



The  $^{13}\text{C}$  shift observed for the two central carbons in this ion is  $\delta_{^{13}\text{C}}$  197.2 and the proton coupled spectrum consists of a doublet ( $J_{\text{CH}} = 65 \text{ Hz}$ )<sup>28)</sup>. If the ion is a rapidly equilibrating pair of ions, the observed shift will be the average of the shifts at the two sites. A good model for estimating these shifts is the methyl  $^{13}\text{C}$  shift and the central  $^{13}\text{C}$  shift in the *t*-butyl cation. The average of these shifts is  $\delta_{^{13}\text{C}}$  187.6. The effect of the two additional methyl groups would be expected to deshield slightly both shifts from those in the model compound, and thus the predicted and observed shift for the rapidly equilibrating pair of ions are in excellent agreement. The coupling constant can also be estimated, again using the *t*-butyl cation as a

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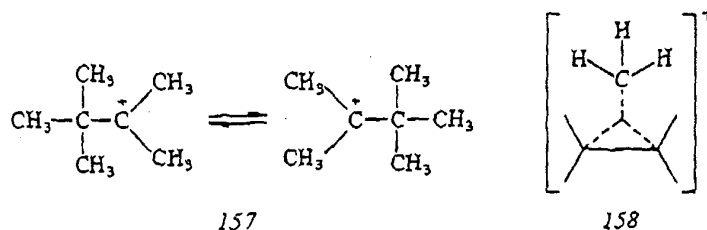
model compound, from the direct and long range C-H coupling constants. The average of these values (assuming the long-range coupling to be negative as is usual in three-bond CCH coupling) is 64 Hz, again in excellent agreement with the observed value. The agreement of both the coupling constant and chemical shift with those predicted for the rapidly equilibrating ion are so good as to leave little doubt as to the nature of this ion. Laser Raman spectroscopy study of the ion also confirms this conclusion. Whereas NMR study of rapidly equilibrating ions is thus possible, clearly the relatively slow time-scale of the NMR experiment does not allow direct, separate observations of individual molecules, but gives information through analysis of *average* chemical shift and coupling constants of the equilibrating species. Thus clearly the need arises to apply physical methods to the study of these ions, the time scale of which is such, that it will not be affected by even the fastest chemical equilibrating processes.

We consequently undertook the infrared and Raman<sup>26, 34)</sup> spectroscopic study of the tetramethylethyl cation 154 and for comparisons a series of alkyl cations with known "static" structure, such as the *t*-butyl, *t*-amyl, and isopropyl cations 1, 3 and 2. The nearly identical spectra of the ions and the evident planarity (or close to planarity) of the carbocation centers suggest that the tetramethylethyl cation is "classical", similar to the static ions used for comparison.

Finally perhaps the most decisive physical method yet applied to the study of carbocations in the condensed state is that of X-ray photoelectron spectroscopy (ESCA) which allows to differentiate equilibrating trivalent carbocations from bridged ions<sup>38)</sup>. This method allows direct measurement of carbon 1s electron binding energies. As the charge distribution within carbocations causes increasing binding energies with increasing positive charge localization, highly electron deficient classical alkyl and cycloalkyl cation centers (such as in the *t*-butyl and *t*-amyl cations) show about 4 eV 1s binding energy differences from the remaining less electron positive carbon atoms. In five coordinated bridged carbocations (see subsequent discussion of the norbornyl cation) there is no such highly electron deficient carbon center indicated by the photoelectron spectra. The ESCA spectrum of the tetramethylethyl cation 154 shows an identical separation (1s  $E_b$  energies) between  $C^+$  and C as in the *t*-amyl cation 3 (~4.2 eV). As the photoelectron spectra represent observation of the ejected core electron from a single species, no time scale limitation related to possible chemical equilibration phenomena can exist. The photoelectron spectra thus indicate that the ion studied is a classical carbocation and not a bridged tetramethyletheneprotonium ion 156 (which corresponds to the transition state of the equilibration process or may also be a high lying intermediate).

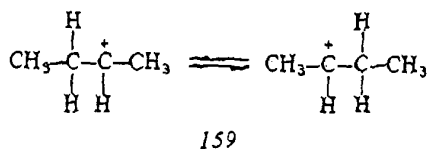
An example of an equilibrating or methyl bridged ion is the *pentamethylethyl cation* (*triptyl cation* 157. The proton NMR spectrum consist of a single resonance at  $\delta$  2.90<sup>47)</sup>. This chemical shift was considered indicative of a rapidly equilibrating structure rather than the bridged structure although the fact that only a single proton resonance is observed does not enable these structures to be distinguished since in the methyl bridged carbocation equilibration of the methyls via the two classical ions as intermediates would be expected to occur. As in the case of the tetramethylethyl cation 154 the  $^{13}C$  NMR spectral data can give additional evidence for the structure<sup>31)</sup>.

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The average  $^{13}\text{C}$  shift for  $\text{C}_2$  and  $\text{C}_3$  was found to be  $\delta_{\text{C}_{13}}$  205.3 ppm consistent only with the rapidly equilibrating structure. The norbornyl cation (vide infra) provides an experimentally observed model for the methyl bridged ion (the bridged carbon showing a CMR shift of 21.8) which would on this basis be expected to give a shift of 100 ppm more shielded than that actually observed. Since this ion is equilibrating, the observed coupling will be the average of the two and three bond proton-carbon coupling constants. The two bond coupling constant in *n*-butyl cation is 6.5 Hz and a similar value would be expected in this ion. For the observed coupling constant to be zero, the three bond coupling must therefore have the same magnitude but opposite sign. Although the signs for only a few such couplings have been determined, such a sign alternation has been reported by Karabatsos, the two bond coupling being negative and the three bond coupling positive.

The proton spectrum of the *sec*-butyl cation at  $-120^\circ$  consists of two resonances at  $\delta$  3.2 and  $\delta$  6.7 of relative area 2 : 1<sup>195</sup>. This is a result of a degenerate 1,2 hydride shift which at this temperature is fast with respect to the NMR time-scale.



The  $^{13}\text{C}$  spectrum of the two central carbons was found to be a quartet at  $\delta_{13\text{C}}$  172.6, with a carbon-hydrogen coupling constant of  $70 \pm 2 \text{ Hz}$ <sup>31</sup>. Using the shifts observed in the tetramethylethyl and pentamethylethyl cations 154 and 157 as models for the effect of methyl substitution in equilibrating ion (8 ppm) leads to a predicted shift of  $\delta_{13\text{C}}$  181. Using the isopropyl cation as a model gives an estimated coupling constant of 72 Hz. As in the two previous examples the  $^{13}\text{C}$  evidence demonstrates that the *sec* butyl cation 159 is an equilibrating "classical" carbocation although some contribution by the bridged "non-classical" cation seems possible.

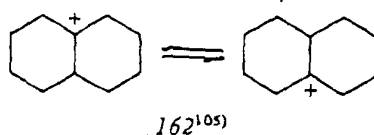
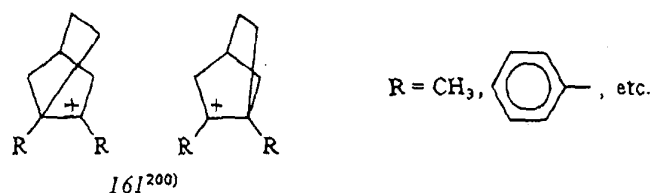
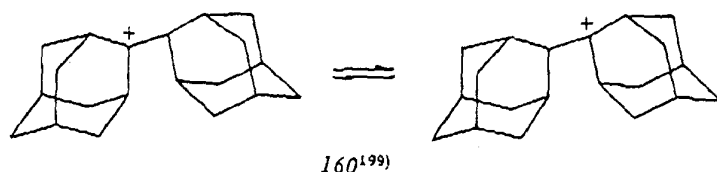
Recently with Donovan we have determined<sup>32</sup> the methyl substituent effect  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  to the carbocation center in  $\text{C}_3$  to  $\text{C}_8$  alkyl cations. From these values it was possible to estimate the  $^{13}\text{C}$  NMR shifts of tertiary-tertiary and secondary-secondary equilibrating ions. The results agreed well with experimentally obtained values in the case of tertiary-tertiary equilibrating ions, but with secondary-secondary equilibrating systems major deviations were observed. This indicates the contribution of partial hydrogen bridged structures in secondary-secondary equilibrating ion such as 159.



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Saunders et al. have reported isotope induced splitting of shifts in the proton NMR spectra of tetramethylethyl<sup>196)</sup> and pentamethylethyl cations<sup>197)</sup> 154 and 157 where deuterium in the methyl groups perturb the equilibria. The observed splittings clearly reinforce the classical nature of these ions. This ingenious isotopic perturbation of resonance technique has been extended<sup>197)</sup> to <sup>13</sup>C NMR spectroscopy where the larger-chemical shifts observed enhances the sensitivity. From these splittings it is possible to differentiate a equilibrating classical ion from a non-classical one.

The proton spectrum of *cyclopentyl cation* 37 in SbF<sub>5</sub>-SO<sub>2</sub>-ClF solution at -70°, as mentioned previously, consists of a singlet at  $\delta$  4.68. The <sup>13</sup>C satellites from this peak show a  $J_{CH}$  coupling constant of 28.5 Hz and have an intensity five times that normally observed. This is a result of the degenerate rearrangements that occur in this ion which, on the NMR time-scale, leading to complete equilibration of the nine protons around the five carbon atoms. The <sup>13</sup>C spectrum is a 10 line multiplet at  $\delta_{13C}$  98.4 with a coupling of 28.5 Hz<sup>31)</sup>. (Fig. 12). Again ESCA study<sup>38)</sup> of the ion shows the presence of a secondary carbocation center separated by ~ 4.8 eV from the additional carbon atoms. There is by now a whole host of equilibrating classical and partially bridged ions reported in the literature<sup>199-201)</sup>. Some of the representative examples are:

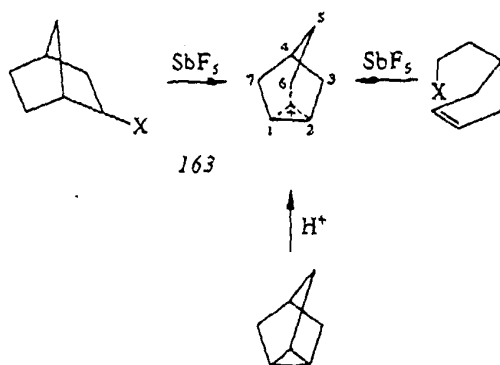


## 21. Norbornyl Cations

Consideration of the cyclopentyl cation is leading us to the discussion of one of the most controversial of all carbocations, the *norbornyl cation*, 163 around which the structure the much publicized classical-nonclassical controversy of "carbonium ions" mainly centered in recent years<sup>9)</sup>.

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The methods that we worked out in the early 1960's to generate and observe stable carbocations in low nucleophilicity solutions<sup>2)</sup> were successfully applied to direct observation of the norbornyl cation. Preparation of the ion by the "σ route" from 2-norbornyl halides, by the "π route" from β-Δ<sup>3</sup>-cyclopentenylethyl halides, and by the protonation of nortricyclicene all led to the same norbornyl cation.



The method of choice for preparation of the norbornyl cation (giving the best resolved NMR spectra, free of dinorbornylhalonium ion equilibration), is from *exo*-2-fluoronorbornane in  $\text{SbF}_5\text{--SO}_2$  (or  $\text{SO}_2\text{ClF}$ ) solution. With Saunders and Schleyer in a joint effort we first investigated the 2-norbornyl cation in 1964<sup>202)</sup> and observed its  $^1\text{H}$  NMR spectrum, having prepared the ion from *exo*-2-fluoronorbornane in  $\text{SbF}_5\text{--SO}_2$ . At room temperature the  $^1\text{H}$  NMR spectrum consisted of a single broad band at  $\delta$  3.75 (Fig. 12) due to scrambling of all hydrogen atoms. The contrast between this single band and the complex spectrum of the progenitor, 2-*exo*-fluoronorbornane, is striking. The equilibration of the hydrogen atoms is caused by fast 3,2- and 6,1,2-hydrogen shifts and by Wagner-Meerwein rearrangement.

Similarly at room temperature the  $^{13}\text{C}$  spectrum of the ion shows a single broad absorption line centered at  $\delta_{13\text{C}}$  59.8 (from external  $\text{Me}_4\text{Si}$  to which all shifts are related). When the temperature was lowered to  $-70^\circ\text{C}$  the  $^1\text{H}$  NMR spectrum of the

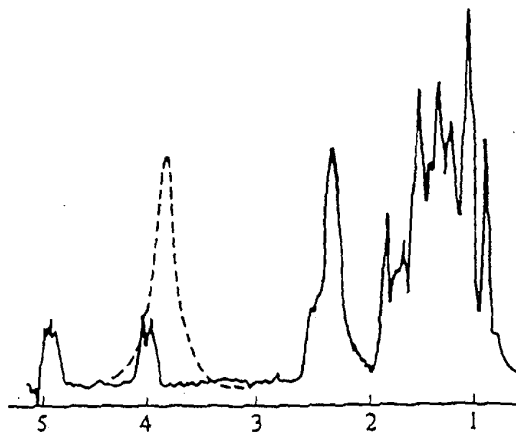


Fig. 12.  $^1\text{H}$  NMR spectrum (60 MHz) of the norbornyl cation at  $35^\circ\text{C}$  (dotted line) and the precursor 2-*exo*-fluoronorborane (full line)

## The Search of Stable Carbocations

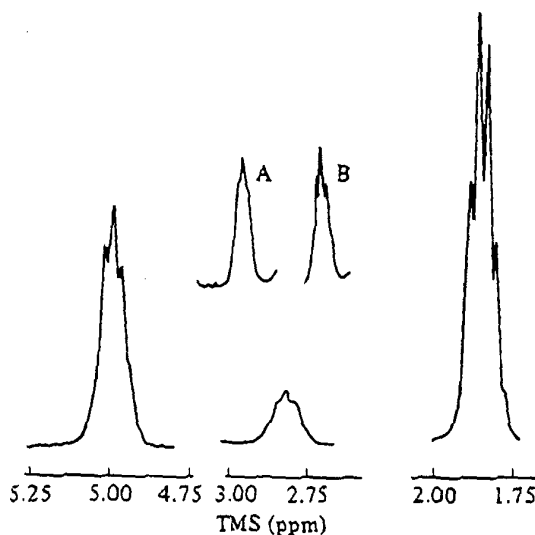


Fig. 13.  $^1\text{H}$ -NMR spectrum (100 MHz) of the norbornyl cation in  $\text{SbF}_5\text{-SO}_2$  solution at  $-80^\circ\text{C}$ . The insert shows the effect of irradiating the low-field septuplet on the one-proton peak at  $\delta$  2.82. A is the spectrum without irradiation and B is with irradiation

2-norbornyl cation resolved into three peaks with relative areas 4 : 1 : 6 (Fig. 13). The spectrum did not change when the temperature was further lowered to  $-120^\circ\text{C}^{10}$ . Jensen and Beck obtained in  $\text{GaBr}_3\text{-SO}_2$  similar spectra of good resolution<sup>203</sup>.

The spectrum was interpreted as evidence that the 3,2-hydrogen shift was frozen out, but the 6,1,2-hydrogen shift and the Wagner-Meerwein rearrangement are still fast even at the low temperature used ( $-120^\circ\text{C}$ ). The rate of the slow 3,2-hydrogen shift was established from temperature-dependence studies, by comparing experimental spectra with those calculated for different rates. The activation energy of this shift is  $10.8 \pm 0.6$  kcal/mol, with  $A = 10^{12.3} \text{ sec}^{-1}$ <sup>27</sup>.

When the ion is prepared at  $-78^\circ\text{C}$  in  $\text{FSO}_3\text{D-SbF}_5\text{-SO}_2$  solution from nortri-cyclane, only one deuterium atom is incorporated, and in the  $^1\text{H}$  NMR spectrum the relative area of the low-field peak is reduced from 4 to 3. No further inter- or intra-molecular scrambling of the deuterium is observed during 1 h at  $-78^\circ$ .

Preparation of the norbornyl cation by protonating nortricyclane, or from reaction of norbornyl fluoride or alcohol with  $\text{SbF}_5$ , precludes equilibration involving dinorbornylhalonium ions, but that complication can occur under certain conditions between norbornyl chloride or bromide and the norbornyl cation. We have studied equilibration of the norbornyl cation with excess norbornyl halides through the dinorbornylhalonium ions, and described its characteristics.

Subsequently we succeeded in "freezing out", on the NMR time scale, the fast 6,2-hydrogen shift<sup>10</sup>. Using a mixed  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  solvent system, we could observe the 100-MHz spectrum at temperatures down to  $-156^\circ\text{C}$ . At  $-120^\circ\text{C}$ , the spectrum was identical to that described at  $-78^\circ\text{C}$ , but between  $-128$  and  $-150^\circ\text{C}$  significant changes in the spectrum occurred. The low-field peak due to the four equilibrating "protonated cyclopropane" ring protons broadened and then separated into two resonances, each of relative area two, at  $\delta$  3.05 and 6.59. The high-field resonance due to the six methylene protons broadened, developing a shoulder at  $\delta$  1.70. The peak at  $\delta$  2.82 due to the bridgehead proton remained un-

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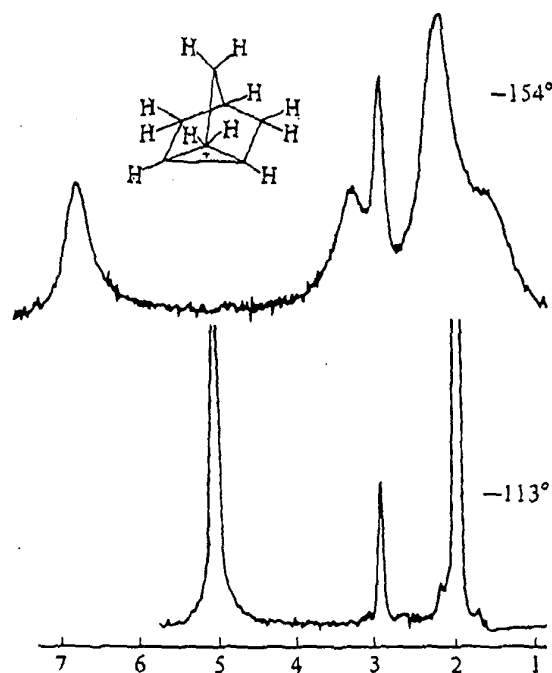


Fig. 14.  $^1\text{H}$ -NMR spectra (100 MHz) of the "norbornyl cation" in  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  solution at temperatures between  $-113$  and  $-154^\circ\text{C}$

changed (Fig. 14). The temperature dependence of the low field resonance was used to calculate rate constants; the activation energy was  $5.9 \pm 0.2 \text{ kcal/mol}^{-1}$  and the pre-exponential factor  $10^{12.7} \text{ sec}^{-1}$ .

These observations could be consistent with either of two interpretations:

- (a) that the ion is classical and that the temperature dependence corresponds to the "freezing out" of the 6,1,2-hydrogen shift, the Wagner-Meerwein rearrangement still being fast at  $-156^\circ$ ; or
- (b) that the ion is nonclassical, all rearrangements have been "frozen out", the structure of the ion being that of the methylene bridged pentacoordinated ion.

In order to differentiate between these two possibilities the Raman and  $^{13}\text{C}$  NMR spectra of the ion were studied<sup>10</sup>. As Raman spectroscopy is a fast physical method (assuming that vibrational transition rates are faster than any of the hydrogen or alkyl shifts) and the question of possible equilibration versus bridged ion is unimportant. The previously discussed technique of average  $^{13}\text{C}$  NMR shifts should be also applicable in this case to differentiate a static nonclassical bridged ion from rapidly equilibrating classical carbenium ions.

The Raman spectroscopy study of the stable norbornyl cation was carried out using a He-Ne laser. In the C-C stretching frequency region there is only one strong line at  $972 \text{ cm}^{-1}$  ( $\rho = 0.35$ ). The C-H stretching frequency region shows five lines, one of which is at  $3110 \text{ cm}^{-1}$ . The skeletal vibrations of the ion and comparison with model compounds suggest a structure closely related to nortricyclicene, but not to norbornane, e. g. the bridged ion of protonated nortricyclicene nature.

Carbon-13 spectroscopy provides even more convincing evidence for the structure of the norbornyl cation. Using first (with White) the INDOR method<sup>10</sup> and later (with Liang) the fast Fourier transformation method<sup>10</sup>, we obtained the com-

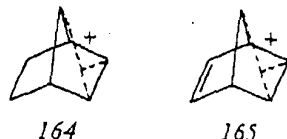
## The Search of Stable Carbocations

plete  $^{13}\text{C}$  NMR spectrum, with all the coupling constants and multiplicities both at  $-70^\circ\text{C}$  under conditions of rapid equilibration of the norbornyl cation, and at  $-150^\circ\text{C}$  as the static "frozen out" ion. The results are summarized in Table 5.

The proton-decoupled FT  $^{13}\text{C}$  NMR spectrum of the ion at  $-70^\circ\text{C}$  consists of three carbon resonances at  $\delta_{13\text{C}}$  92, 37.7 and 31.3, for equilibrating C.1, C.2, C.6, bridgehead C.4, and equivalent methylene carbons (C.3, C.5, and C.7), respectively. (Assignments were made by the off-resonance  $^{13}\text{C}$  NMR spectrum.) The most deshielded carbon resonance ( $\delta_{13\text{C}}$  92) shows a quintet indicating that each of the cyclopropane-like ring carbons couples with four equivalent protons, while the bridgehead carbon resonance and the methylene carbon resonance are a doublet and triplet, as they are coupled with one and two protons, respectively. At lower temperatures ( $-150^\circ\text{C}$ ) this resonance is separated into two components at  $\delta_{13\text{C}}$  125.3 (for C.1 and C.2) and 22.4 (for C.6). The bridgehead carbon (C.4) resonance is slightly moved to higher field at  $\delta_{13\text{C}}$  33.4. The methylene resonance is also separated into two component at  $\delta_{13\text{C}}$  48 (for C.3 and C.7) and 28 (for C.5). The C-H coupling constants ( $J_{\text{CH}}$ , in Hz) given in Table 5 were obtained directly from the proton-coupled  $^{13}\text{C}$  NMR spectrum. The pentacoordinated bridging methylene carbon atom is not deshielded ( $\delta_{13\text{C}}$  22.4), whereas the tetracoordinated carbons to which bridging takes place (and which consequently carry more positive charge) show more deshielding ( $\delta_{13\text{C}}$  125.3), but are still much more shielded than expected for an equilibrating classical ion.

In the proton-coupled  $^{13}\text{C}$  NMR spectrum of the norbornyl ion no coupling was observed between the methylene hydrogens at the pentacoordinated carbon (C.6) and the cyclopropane-like carbons (C.1 and C.2). This is expected from the non-classical structure since the two-electron, three-center bonds are longer and weaker than normal  $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}$  bonds.

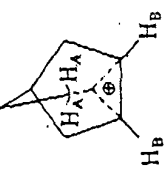
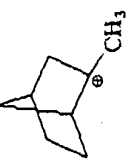
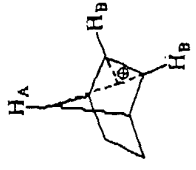
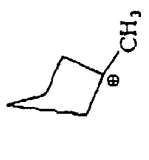
The  $^{13}\text{C}$  NMR spectra show that the norbornyl cation is a nonclassical carbonium ion with a pentacoordinated bridging carbon atom. The magnitude of  $J_{\text{C.6--H}} = 145.8$  Hz in the 2-norbornyl cation is smaller than those for  $J_{\text{C.1--H}}$  in the 7-norbornenyl and 7-norbornadienyl ions 164 and 165 (218.9 and 216.4 Mz. respectively)<sup>10</sup>. This is expected as the strained C.7 carbons in the latter have higher s character in the C-H bonds than has C-6 in the former (for an  $\text{sp}^3$  carbon  $J_{\text{CH}}$  is about 125 Hz, corresponding to 25% s character). An increase of s character associated with the C-H bond is expected to increase the C-H coupling constant. Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate that the bridging pentacoordinated methylene carbon C.6 in the norbornyl ion is tetrahedral in nature and carries little positive charge.



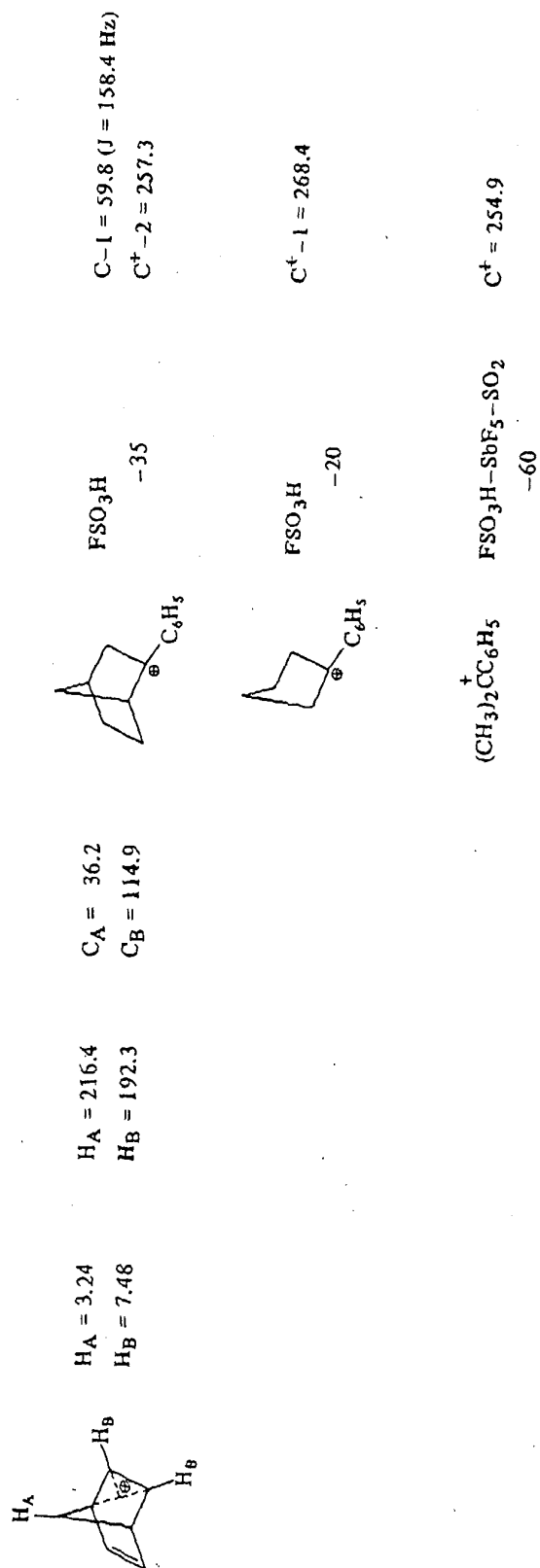
In a ESCA study with Mateescu and Riemenschneider<sup>38</sup> we also succeeded to observe the ESCA spectrum of the norbornyl cation and compared it with that of the 2-methylnorbornyl cation and other trivalent carbenium ions, such as the cyclopentyl and methylcyclopentyl cations. The 1s electron spectrum of the norbornyl

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Table 5. Comparison of the NMR parameters of the carbocation centers

Ion	Carbocation $\delta$ [ppm]	$J_{CH}$ [Hz]	$\delta_{13C}$ [ppm]	Ion	Carbocation solvent $T$ [°C]	$\delta_{13C}$ [ppm]
	$H_A = 3.05$ $H_B = 6.59$	$H_A = 145.8$ $H_B = 184.5$	$C_A = 22.4$ $C_B = 125.3$		$FSO_3-H-SbF_5-SO_2$ -80	$C-1 = 80.8$ ( $J = 169.5$ Hz) $C^+-2 = 271.1$
	$H_A = 3.25$ $H_B = 7.04$	$H_A = 218.9$ $H_B = 193.8$	$C_A = 34.0$ $C_B = 125.9$		$SbF_5-SO_2$ -60	$C^+-1 = 335.8$
				$(CH_3)_3C^+$	$SbF_5-SO_2ClF$ -60	$C^+ = 335.2$
				$(CH_3)_2CH^+$	$SbF_5-SO_2ClF$ -60	$C^+ = 320.6$

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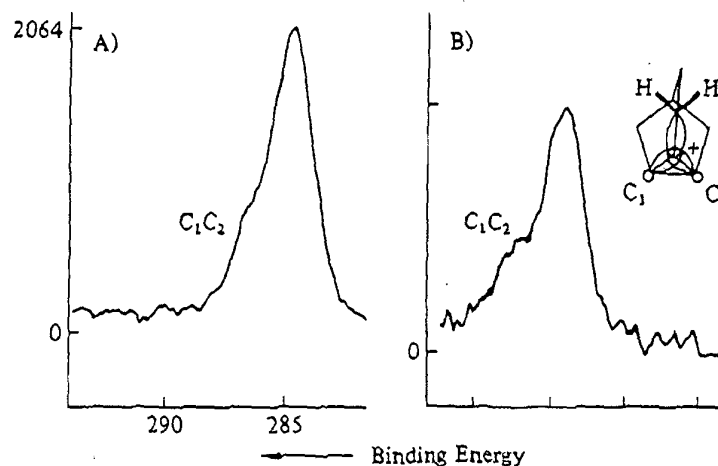


Fig. 15. Carbon 1s photoelectron spectrum of the norbornyl cation: (A) 100-V, (B) 30-V analyzer energy

cation (Fig. 15) shows no high binding energy carbenium center and a maximum separation of less than 1.5 eV between the two "cyclopropyl" type carbons, to which bridging takes place from the other carbon atoms (including the penta-coordinated bridging carbon). The 2-methylnorbornyl cation in contrast shows a high binding energy carbenium center, slightly delocalized, as indicated by the  $\delta E_b$   $\sim 3.7$  eV separation from the other carbon atoms, as do other trivalent carbenium ions. ESCA shift differences are summarized in Table 6.

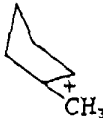
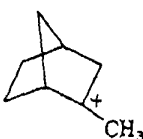


Since in electron spectroscopy the time scale of the measured ionization processes is on the order of  $10^{-16}$  sec, definite ionic species are characterized, regardless on their possible intra- and intermolecular interactions (e. g., Wagner-Meerwein rearrangements, hydride shifts, proton exchange, etc.). Thus, electron spectroscopy gives an undisputable, direct answer to the long debated question of the "non-classical" nature of the norbornyl cation independent of any possible equilibration process.

The bridging methylene carbon in the norbornyl ion is pentacoordinated. It is bound to the hydrogen atom and a carbon atom by two-electron single bonds. The remaining  $sp^3$  orbital is involved in two-electron three-center bond with  $C_1$  and  $C_2$ . It should be pointed, however, that if a highly  $\sigma$ -delocalized but somewhat unsymmetrical non-classical ion would be in a degenerate equilibration process through the completely symmetrical non-classical ion (such as 163) for all practical purposes such systems would show symmetrical nature in the NMR or even ESCA spectra. Thus, the double energy minima would be indistinguishable from a single minimum, as the interconversions would take place through a very low energy barrier, i. e.  $< 2$  kcal/mole. The question is not the possible equilibration between classical ions vs. the symmetrical bridged nonclassical ion, which is ruled out by direct, spectroscopic studies of the long lived ion, but of possibly still equilibrating nonclassical  $\sigma$ -delocalized, but somewhat unsymmetrical ions (double minima) vs. the symmetrical nonclassical ion (single minimum). These are becoming by necessity indistinguishable by usual studies. It is important to recognize that  $\sigma$ -delocalized nonclassical




## The Search of Stable Carbocations

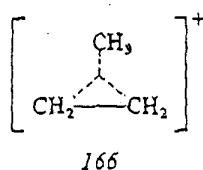
Table 6. Binding energy differences of carbocation centers from neighboring carbon atoms ( $dE_B + C-C$ )

Ion	$dE_B + C-C$	Approximate relative $C^+/C$ intensity
$(CH_3)_3C^+$	$3.9 \pm 0.2$	1/3
	$4.2 \pm 0.2$	1/5
	$3.7 \pm 0.2$	1/7
	$4.8 \pm 0.5$	1/4
	$1.5 \pm 0.2$	2/5

ions are not necessarily only static symmetrically bridged species, contrary to claims made to this effect<sup>9f, h</sup>).

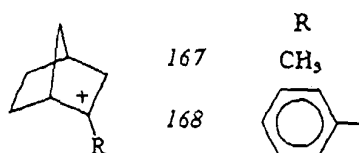
Other examples of directly observed long-lived norbornyl ions in which the tetra- and/or pentacoordinated carbons were identified by NMR spectroscopy are the 7-norbornenyl and 7-norbornadienyl cations<sup>10, 204-209</sup> 164 and 165.

The carbonium centers in the norbornyl cation, 7-norbornenyl cation and 7-norbornadienyl cation<sup>10, 207</sup>) are similar and related to the ethenemethonium ion, 166 although strain differences in the ions are obviously significant. All contain a  two electron three-center bond. The bridging carbon atoms are pentacoordinated, whereas the carbons to which they bridge are tetracoordinated carbenium atoms.



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It is also instructful to discuss studies on 2-methyl- and 2-phenyl-2-norbornyl cations, 167 and 168, both of which have been investigated by proton<sup>10, 210</sup> and carbon-13<sup>211</sup> NMR spectroscopy. The 2-methyl-2-norbornyl cation can be characterized as a partially  $\sigma$ -bond (i. e., C.1—C.6) delocalized carbenium ion, while the 2-phenyl-2-norbornyl cation exhibits the properties of a classical carbenium ion with no significant  $\sigma$  delocalization (of course the positive charge is extensively delocali-



zed into the phenyl  $\pi$  system). These conclusions are particularly supported by comparing C.1 and C.2 carbon resonances in these two ions; the <sup>13</sup>C NMR shifts are shown in Table 2 along with their assignments. The difference in C.2 carbon resonances in the two ions is  $\Delta\delta_{13C} = 271.1 - 257.3 = 13.8$ , while the same difference between the related model cyclopentyl cations is 57.8. Also the carbon shift at the carbocationic center in the 2-methyl-2-norbornyl cation is about 64 ppm less de-

R	$\delta_{13C^+}$
CH <sub>3</sub>	335.8
C <sub>6</sub> H <sub>5</sub>	278.0

shielded than that in the 1-methyl-1-cyclopentyl cation, while the carbon shifts are comparable in the corresponding phenyl substituted ions. These model ions are evidently classical carbenium ions without significant  $\sigma$ -bond delocalization. The discrepancy observed is explained in terms of partial  $\sigma$ -bond delocalization through the C.1—C.6 bond toward the empty 2p orbital at C.2 in the 2-methyl-2-norbornyl cation. Such delocalization is, however, much more profound in the parent, unsubstituted 2-norbornyl cation.

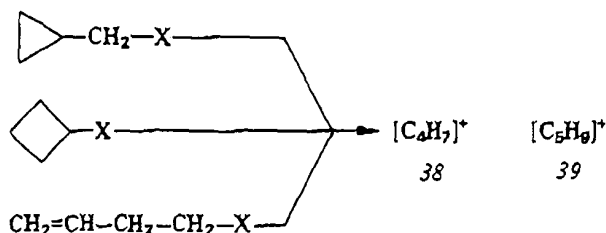
Farnum and Wolf<sup>211b</sup>) studied the relationship between <sup>1</sup>H NMR shifts and substituent effect in a series of substituted 2-aryl-2-norbornyl cations. With substituents increasingly more electron withdrawing, the "onset" of C.1—C.6  $\sigma$  bond-delocalization or nonclassical stabilization was observed, due to increasing electron demand compared to the parent 2-phenyl-2-norbornyl cation, by a gradual and clear change of the NMR patterns. This effect has been recently studied with Prakash and Liang more thoroughly by <sup>13</sup>C NMR spectroscopy<sup>212</sup>, as well as by Farnum<sup>213</sup>. It can be concluded that the original views of Winstein<sup>208</sup>) on the nonclassical nature of the norbornyl cation, based on kinetic and stereochemical results, were fully substantiated through the direct spectroscopic studies of the long-lived ion<sup>10</sup>), which helped to develop our general understanding of carbonium ions, as distinct and well differentiated species from trivalent carbenium ions.

## 22. Cyclopropylmethyl and Cyclobutyl Cations

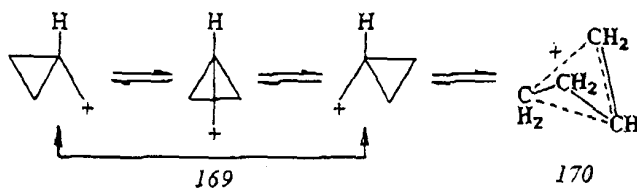
Extensive experimental and theoretical work has been devoted to study the nature of cationic intermediates involved in cyclopropylmethyl, cyclobutyl and homoallylic

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interconversions under both solvolytic and stable carbocationic conditions<sup>2, 91, 214-215</sup>). The non-classical nature of parent cyclopropylmethyl and 1-methylcyclopropylmethyl cations **38** and **39** is now firmly established<sup>94-97</sup>).



Ion **38** (Fig. 16) could be generated both from cyclobutyl and cyclopropylmethyl precursors. At lowest temperatures studied ( $= 140^\circ$ ), ion **38** is still an equilibrating mixture of bisected  $\sigma$ -delocalized cyclopropylcarbinyl cations **169** and the bicyclobutonium ion **170**.



From the comparison of calculated NMR shifts, the low lying species is considered to be bicyclobutonium ion **170**<sup>95</sup>). However, in the case of  $\text{C}_5\text{H}_9^+$  **39**, the low lying species are the methylbicyclobutonium ions **171** with no contribution from either

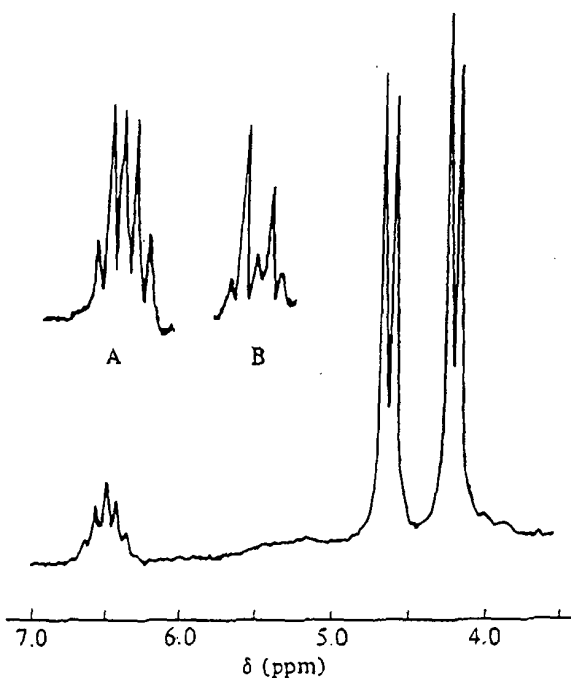
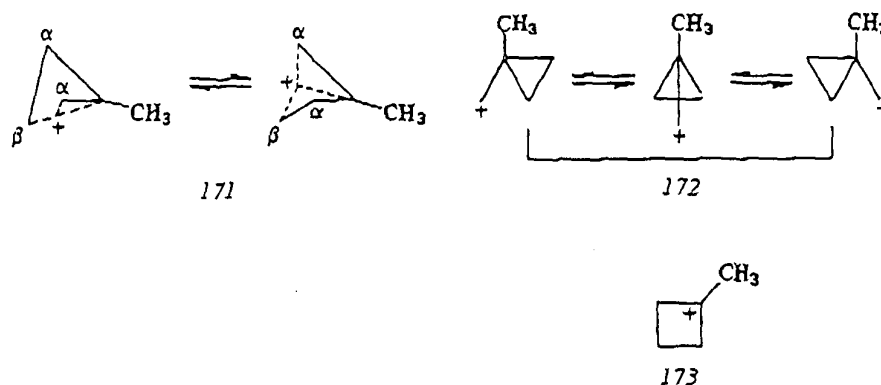


Fig. 16. 100-MHz pmr spectrum of of the cyclopropylcarbinyl cation in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution at  $-80^\circ$ : (A) 60 MHz spectrum of CH-region; (B) 60 MHz spectrum of the CH-region of ion obtained from a  $\alpha,\alpha$ -dideuterio-cyclopropylcarbinyl precursor

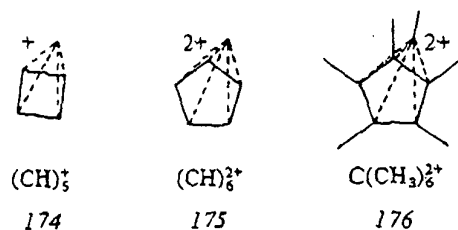
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the bisected  $\sigma$ -delocalized 1-methylcyclopropylmethyl cation 172 or the 1-methylcyclobutyl cation 173, even at the lowest temperature studied ( $= -158^\circ$ )<sup>97</sup>. The observation of the highly shielded  $\beta$ -methylene carbon at  $\delta^{13}\text{C} -2.83$  is particularly convincing evidence for the non-classical bicyclobutonium structures.



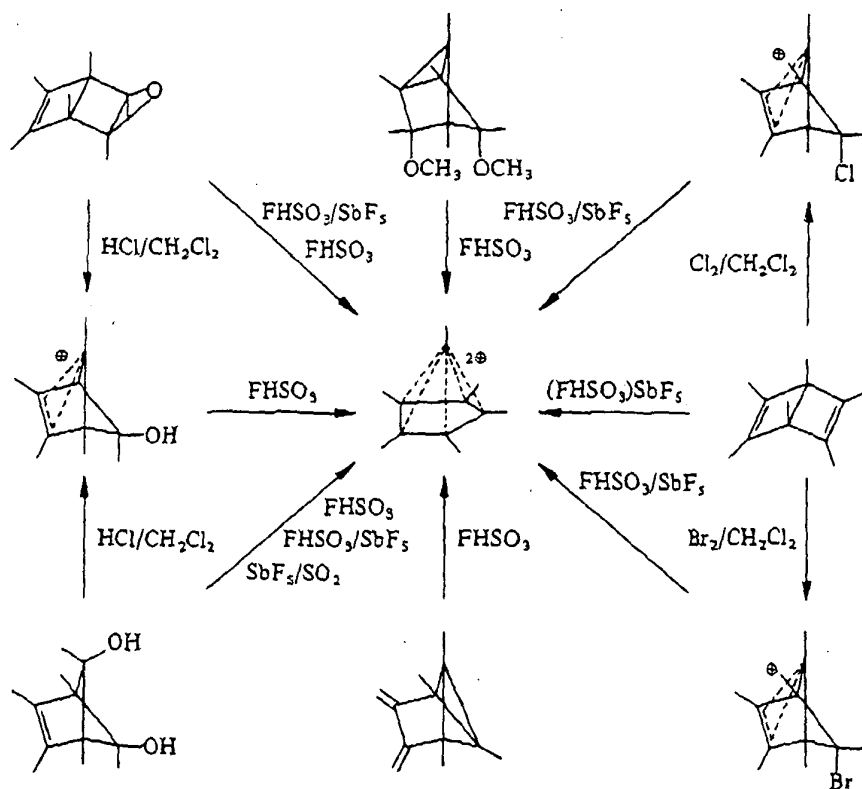
### 23. Miscellaneous Non-Classical Ions

*a. Pyramidal Cations.* Interest is increasing in the preparation, chemistry, and unusual bonding properties of pyramidal carbocations, fascinating newcomers to the non-classical ion group<sup>11, 216-224</sup>. Representatives of two possible types of these ions,  $(\text{CH})_5^+$ , and  $(\text{CH})_6^{2+}$  have already entered the literature. The parent  $(\text{CH})_5^+$  ion has been the subject of a number of calculations<sup>216</sup>, and a methyl substituted derivative has been prepared<sup>217</sup>. Preparative work on several substituted homo-<sup>218</sup> and bishomo- $(\text{CH})_5^+$  cations<sup>219</sup> has also been reported.

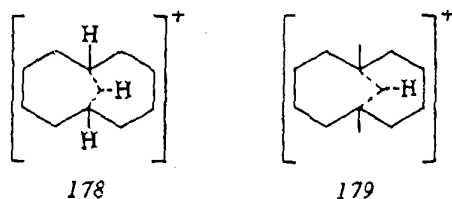


The hexamethyl derivative  $(\text{CCH}_3)_6^{2+}$  a pyramidal dication 176 has been prepared by Hogeveen in superacidic solutions from a variety of precursors<sup>220</sup>. A number of arguments, including NMR spectroscopic evidence and the chemical reactivity justify expression of a strong preference for the nonclassical structure, rather than a rapidly equilibrating system of classical ions (see Fig. 18)<sup>221</sup>. The latter would be expected to show no absorption characteristic of a cyclopropylmethyl system. No such absorption was, however, observed<sup>11</sup>. The nonclassical structure was also substantiated by *ab initio* quantum mechanical calculations on the parent ion<sup>223</sup>.

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b. *Hydrogen Bridged Cyclodecyl Cations.* Sorensen et al.<sup>225)</sup> have recently demonstrated that at very low temperature cyclodecyl cations 177 exists with static, frozen out, 1,6- $\mu$ -hydride structure 178. Similar behaviour was also observed for 1,6-dimethyl analog 179.



The bridging hydrogen in ion 178 is observed at a unusually high field of  $\delta -6.85$  as compared to the adjacent methine protons ( $\delta 6.80$ ).

c. *Trishomocyclopropenium and Analogous Ions.* Following Winstein's proposal<sup>226)</sup> of the formation of the trishomocyclopropenium ion 180 in the solvolysis of *cis*-bicyclo [3.1.0] hexyltosylate, extensive effort was directed towards its generation under stable ion conditions<sup>227)</sup>. Masamune et al.<sup>228)</sup> were successful in generating ion 180 and its ethanobridged analog 181 from the corresponding *cis*-3-chlorobicyclo [3.1.0] hexane and 8-chlorotricyclo [3.2.1.0<sup>2,4</sup>]octane precursors in superacidic media. The  $^{13}\text{C}$  NMR shifts of charged center is unusually shielded indicating

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180



181



182

the non-classical nature of these ions. After unsuccessful earlier attempts ion 180 has also been prepared recently<sup>229</sup> from bicyclo[3.1.0]hexan-3-ol<sup>228</sup>. Another trishomoaromatic ion analog of 180 is the 9-pentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>2,8</sup>.0<sup>5,7</sup>]nonyl cation 182. Coate's<sup>230</sup> ion 182 also has three fold symmetry and its <sup>13</sup>C NMR spectrum shows highly shielded shifts for the charged carbons.

#### IV. Significance and Future Outlook

With the advent of superacidic Lewis acid halide (such as SbF<sub>5</sub>, and TaF<sub>5</sub>) and Bronsted acid (such as HF-SbF<sub>5</sub>, FSO<sub>3</sub>H-SbF<sub>5</sub>) systems, a new vista of chemistry has emerged. With methods developed in our laboratories in the early sixties it is possible now to generate as stable long lived species practically any type of carbocations and study their structure and chemical reactivity. These studies also helped in the understanding of the nature of electrophilic reactions and their intermediates. Trivalent carbocations (classical ions) as well penta (or higher coordinated) carbocations are now well established. The concept of pentacoordinated carbocation formation via electron sharing of single bonds with electrophilic reagents in three-center bond formation promises to open up an important new area of chemistry.

Trivalent carbocations as recognized in the pioneering work of Meerwein, Ingold and Whitmore, play an important role in acid-catalyzed hydrocarbon transformation reactions (isomerization, alkylation, cyclization, polymerization, etc.), as well in a large variety of electrophilic reactions including those of the generalized Friedel-Crafts type (generally with  $\pi$ -donor reagents).

On the other hand pentacoordinated carbocations play an equally important role in electrophilic reactions of  $\sigma$ -donor saturated systems.

The realization of the electron donor ability of shared (bonded) electron pairs (single bonds) could one day rank equal in importance with G. N. Lewis' realization of the importance of the electron donor unshared (non-bonded) electron pairs. We can now not only explain the reactivity of saturated hydrocarbons and in general single bonds in electrophilic reactions, but indeed use this understanding to explore new areas of carbocation chemistry.

The generalized concept of carbocations and electrophilic reactions indicates that the initial interactions of electrophiles with  $\pi$ -donor systems (olefins, acetylenes, aromatics) involves three-centered bond carbonium ion formation. The  $\pi$ -bond provides the bonding electron pair which interacts with the empty orbital of the electrophile. Thus in principle there is no difference between the electrophilic reactivity of

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$\sigma$ - and  $\pi$ -bonded systems. Electrophilic reactions thus take place at the involved bonds and only in cases where non-bonded electron pairs are present, at individual atoms.

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